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AN ISOTHERMAL CALORIMETER FOR SLOW REACTIONS[1]

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This calorimeter has been designed for the study of phenomena involving the slow evolution of heat, particularly in the study of chemical kinetics and biological processes. It can be used at different temperatures. The heating effect is exactly counterbalanced by a cooling effect produced by evaporating carbon tetrachloride or other liquid in a regulated air stream. The amount of carbon tetrachloride evaporated is determined by adsorption in silica gel. The increase in weight is converted into calories by calibration with electrical heating. In its present form the calorimeter is limited to a precision of about one per cent, and it is not recommended for rapid reactions with plenty of material where standard calorimeters are now satisfactory.

Endothermic reactions can be measured accurately and easily by balancing with measured electrical heating. Exothermic reactions have been balanced by melting ice at 0°C. as in the Bunsen ice calorimeter, by vaporization of a liquid at its boiling point as in the ether calorimeter (1), by addition of cold water (2), cold mercury (3) or a salt which absorbs heat on solution (4). The Peltier effect existing between two dissimilar metals, when a current of electricity flows, has been used also (5, 6).

DESCRIPTION OF THE CALORIMETER

The calorimeter is shown in figure 1. It consists of two vacuum-walled vessels, I and N, mounted with various accessories on a frame, immersed in a large thermostat 20 cm. below the water level. The vessels are connected by a multiple junction thermel. The "reference" unit I, which stays at constant temperature, contains fine oil of low vapor pressure, an electric heater, and a stirrer. A second thermel (not shown) indicates equality of temperature between the oil and the water of the thermostat.

The "variable" unit N of 400 cc. capacity contains kerosene. The cover of nickel-plated iron sets into a mercury seal shown at F. A ring of sheet iron, held in place with rubber, contains the mercury and the whole seal is protected on the outside with large rubber tubing. Various accessories, passing through small tubes in the cover, are attached with litharge-glycerine cement.

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[1] Further details of this investigation are contained in part of a Ph.D. thesis filed in the Library of the University of Wisconsin by E. D. Coon in January, 1932.

In the first models the whole calorimeter was filled with carbon tetrachloride and short sections of rubber tubing were exposed to the vapor, but it was found that the variable vessel was always a little colder than the thermostat even after standing twenty-four hours. This cooling effect, which persisted no matter whether the room was colder or warmer than the thermostat, was finally traced to solution of the carbon tetrachloride vapor in the rubber and a slow evaporation of the liquid to maintain full vapor pressure.

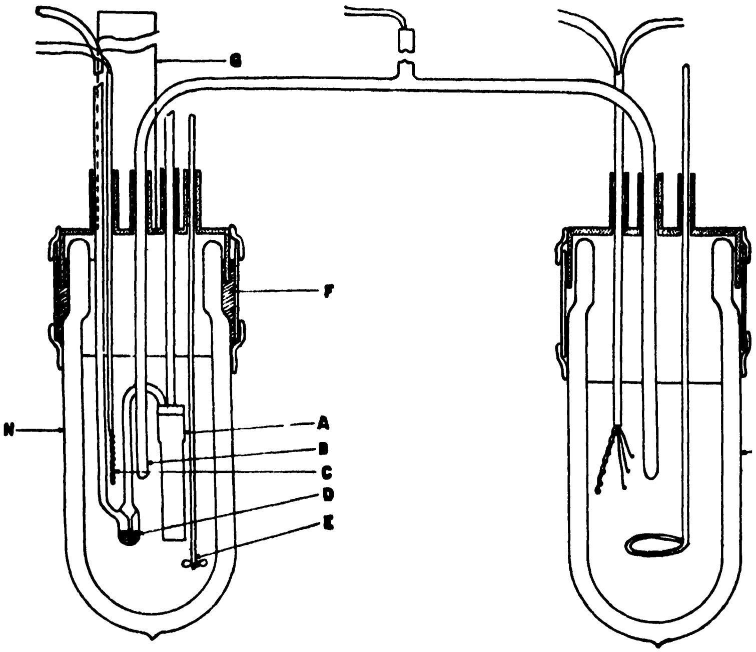

Fig. 1. Isothermal Calorimeter

The thermel B connects with the reference unit. The stirrer E of glass extends through a long bearing to the water level. The glass shaft is cemented to a brass rod which rotates in a bearing several centimeters above the cover. The heat generated in the bearing is prevented by the thermostat from reaching the calorimeter. The chimney G, for the admission of reacting materials, extends to the water level where it is provided with a stopper. The heating coil C of 50 cm. bare No. 28 constantan wire is wound on a glass tube and soldered to leads of No. 16 copper wire. The leads are set in paraffin in long snugly-fitting glass tubes passing through the thermostat water.

The cooling unit A is a cylinder of sheet copper containing carbon tetrachloride through which air is bubbled. Other inert liquids of different vapor pressures may be more suitable under other conditions. For high temperatures a higher boiling liquid is better. The mercury trap D is introduced to insure the same conditions at the beginning and at the end of a determination. A small glass tube (not shown) passes down through the exit tube and ends near the mercury level. By turning a stopcock, air is forced down through this tube and all the vapor beyond the mercury seal is swept out.

The air sent through the cooling unit must be dry and free from any substance which might be adsorbed by the silica gel. The rate of flow is regulated by four stopcocks drawn down to capillaries of different apertures. Connecting these in parallel, it is possible to send air through at any rate from ten to several hundred bubbles per minute. The air is dried by passing it through concentrated sulfuric acid, calcium chloride, phosphorus pentoxide, and silica gel. It is brought to the temperature of the calorimeter by passing through three glass tubes, 2 cm. in diameter and 80 cm. long, filled with copper turnings and immersed in the thermostat. In the last tube is an additional section of phosphorus pentoxide.

The amount of carbon tetrachloride evaporated is determined by adsorbing in two glass-stoppered U-tubes, each containing about 75 grams of silica gel. When the second tube increases in weight by more than about 1 mg. the first tube is rejuvenated by placing in an oil bath at 150° to 170°C. and drawing through dry air for two or three hours.

The thermostat of 750 liters capacity is kept constant within about 0.001° with the help of efficient stirring and a mercury regulator of the oscillating type. The contact wire dipping into the mercury in the capillary is forced up by a spring against the under side of a horizontal pulley wheel. The under side of the wheel is partly cut away so that the contact wire moves up and down for a distance of about 2 mm. during one revolution, thus making and breaking the circuit and insuring certain contact with the mercury.

The thermel, which indicates a difference in temperature between the "variable" and "reference" units, consists of two 11-junction elements. Each is used independently of the other and one acts as a check on the other. Constantan wire (No. 28) and copper wire (No. 24) were used. The resistances of the thermels were 39.92 and 40.29 ohms. When used with the galvanometer, having a sensitivity of 5 mm. per microvolt, a deflection of 1 mm. corresponded to 0.00025°C. The two thermels always agreed within 3 mm. A reversing switch was useful in correcting for possible stray potentials in the circuits. Other switches enabled the operator to use either one of the two thermels or to connect the galvanometer with the potentiometer for use with the heating coil. All connections and switches were well insulated and mounted on grounded copper shields.

PROCEDURE

The thermostat is first brought to the desired temperature (25°C., for example). The reference unit is brought to a temperature slightly lower and the whole calorimeter is set in the thermostat. The temperature of the "reference" is then brought to the temperature of the thermostat by means of the heating coil. The final temperature adjustment is effected simply by means of stirring. The galvanometer is then connected to one of the main thermels connecting the two units, and the temperature of the "variable" unit is brought to the same temperature, using either the heater or the cooler as necessary. These adjustments can be effected in a short time, but in order to insure complete equilibrium the system is left undisturbed for several hours,—preferably over night, when both thermels should read within 0.5 cm. of zero.

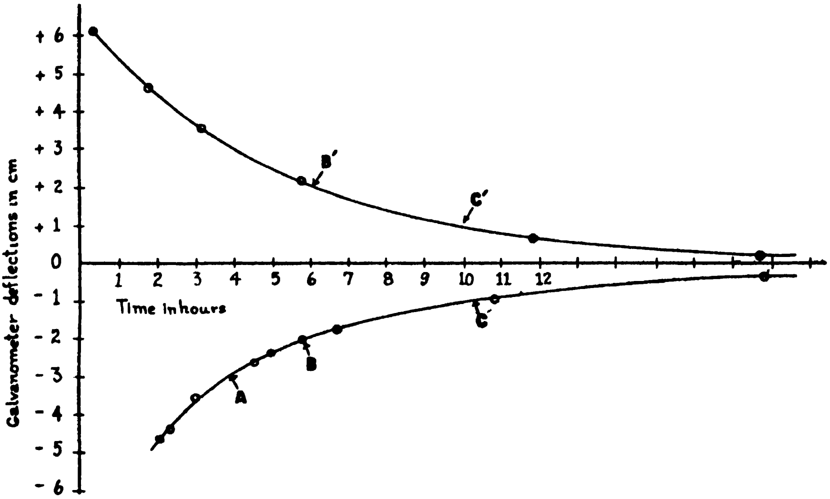

Fig. 2. Rate of Thermal Leakage

Calories per hour A = 0 25, B = 0 12, C = 0 06, B′ = 0 12, C′ = 0.07.

The next step is the establishment of a reproducible condition in the cooler. Air is bubbled through the carbon tetrachloride, and the vapor that passes through the mercury trap is washed out by a stream of air from the inner tube. The temperature is brought back with the heater until the galvanometer reads zero. The silica gel tubes are weighed separately and connected to the outlet of the cooling unit.

The reacting material is then introduced through the chimney, and during the course of the determination the temperature is maintained as nearly isothermal as possible. The galvanometer deflections of the thermel are kept within 3 or 4 cm. of the zero point and the times of the positive and negative deflections are kept about equal. With slow reactions evolving less than 3 or 4 calories per hour this control is not difficult, and with reactions involving more heat the control becomes relatively less important.

At the end of a determination the vapor in the exit tube of the cooler is again swept out and if necessary the original temperature is restored. The silica gel tubes are weighed and the heat of reaction determined by the amount of carbon tetrachloride adsorbed; 0.0206 gram is equivalent to 1 calorie as shown below.

It is easier—and also sufficiently accurate—to apply a small correction at the end of the experiment than to bring back the galvanometer exactly to zero. Experiments with the direct input of electrical heat showed that a deflection of 1 cm. corresponded to 0.357 calorie in the empty calorimeter and to 0.372 calorie when the calorimeter contained reacting material in a certain glass tube.

The errors introduced by thermal leakage when the calorimeter is not exactly balanced, are shown in figure 2. Tangents to these experimental curves give the rates of cooling or heating. A deflection of 1 cm. of the thermel-galvanometer indicates that the temperature of the variable unit differs from that of the reference unit and the thermostat by 0.0025°C., and that the transfer of heat then amounts to 0.06 calorie per hour.

CALCULATIONS

The input of electrical heat was determined by standard methods with a type K potentiometer.

The heat of stirring constitutes the least accurate part of the measurements but the correction is small—about 0.1 calorie per hour. In slow reactions it is necessary to maintain stirring only for a portion of the time, and in more violent reactions the total evolution of heat is large compared with the heat of stirring. After a rapid change in temperature it is necessary to stir for at least ten minutes to insure thermal equilibrium.

The heat of vaporization of carbon tetrachloride

It was not the object, in this investigation, to find the true heat of vaporization but rather to determine the heat of vaporization under the conditions of this calorimeter so that exothermic heats of reactions may be calculated from it. It is possible that a slight Joule-Thompson effect at the mercury trap and some loss of spray have prevented the determination of the true heat of vaporization. Nevertheless the value obtained here is not greatly in error and the method can be adapted easily for exact measurements of the heats of vaporization of liquids at various temperatures.

The carbon tetrachloride was purified by refluxing for 2 hours with potassium dichromate and sulfuric acid. It was fractionally distilled and the portion boiling between 75.18°C. and 75.20°C. at 734.2 mm. was used.

The rate of flow of air through the cooler was adjusted so that the heat absorbed in evaporating the carbon tetrachloride practically offset the electrical heating. The average value of the current through the heating coil was obtained by plotting the current against time and estimating the median height. The value obtained is at least one decimal place beyond significant figures. A small "end correction" was applied for failure to reach complete "isothermality" at the end of a determination.

Several experiments were carried out using a current of about 0.1 ampere for times ranging between fifteen and thirty minutes and evaporating 0.25 to 0.5 gram. It was found that at 25°C. the evaporation of 0.0206 ± 0.0002 gram of carbon tetrachloride is necessary to offset the evolution of 1.00 calorie (15° calorie) of heat. No calorimetric determination of the heat of vaporization of carbon tetrachloride at 25°C. is available in the literature as a check on this value. In fact most heats of vaporization have been determined only at the normal boiling point; a few at 0°C. A value of 0.0200 gram per calorie was obtained from the Clausius-Clapeyron equation, using the vapor pressure data from the International Critical Tables.

Heat of neutralization of hydrochloric acid

The accurately known heat of neutralization of hydrochloric acid by sodium hydroxide was chosen to test the calorimeter, even though such a fast reaction as this can be determined more accurately with other, simpler types of calorimeters. It was thought that a satisfactory check using only 2 cc. of 0.5 *N* hydrochloric acid would give confidence in measuring unknown heats of reaction.

Exactly 2.00 cc. of 0.4942 *N* hydrochloric acid was placed in the thin glass vessel shown in figure 3 and sealed off. A slight excess of 0.5 *N* carbonate-free sodium hydroxide was placed in the upper compartment and the whole vessel was brought to the temperature of the thermostat and then submerged in the calorimeter. When thermal equilibrium was established the tip of the inner tube was broken with a long rod and the upper solution allowed to flow down. Mixing was effected by gentle shaking. The reaction was so rapid that in attempting to keep the temperature constant, too much carbon tetrachloride would often be evaporated. In such cases it was necessary at times to use the heating coil. The results are summarized in table 1. The values in the last column are obtained by subtracting the sum of all the corrections from the calories absorbed by the vaporization of carbon tetrachloride.

Considering the small amount of material used the average value of 13.39 is in very good agreement with the best values in the literature obtained with large quantities. Recalculation of the data of Richards and Rowe (7) and of Richards and Hall (8) and a correction from 0.55 *N* give 13,909 calories for the heat of neutralization per mole in 0.50 *N* solutions at 20°C. Correcting to 25°C. this value becomes 13,642 calories per mole and 2.00 cc. of 0.4942 *N* hydrochloric acid then evolve 13.48 calories when neutralized with 0.50 *N* sodium hydroxide.

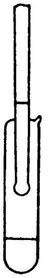

FIG. 3. MIXING VESSEL

TABLE 1

The heat of neutralization of 2 cc. of 0.4942 N hydrochloric acid

WEIGHT CCl_4	CALORIES EQUIVALENT CCl_4	HEATING COIL	TIME OF STIRRING	HEAT OF STIRRING	END CORRECTION	TOTAL CORRECTION	HEAT OF NEUTRALIZATION
gram		*calories*	*minutes*	*calories*	*calories*	*calories*	*calories*
0 4287	20 81	7 196	55	0 11	+0 145	7 45	13 36
0 3701	17 96	4 666	40	0 08	0 20	4 54	13 42
0 2772	13 44	none	40	0 08	0 10	0 18	13 26
0 2886	14 00	1 00	37	0 07	0 48	1 59	13.41
0 3256	15 80	2 67	55	0 11	0 48	2 30	13 50
						Average =	13 39

Heat of hydrolysis of methyl acetate

The reaction $CH_3COOCH_3 + H_2O + (N\ HCl) = CH_3COOH + CH_3OH + (N\ HCl)$ was chosen for study because it is a typical, slow reaction which can be readily followed by titrations. The reaction was catalyzed by normal hydrochloric acid. It is known that the reaction involves very little thermal change because the equilibrium is nearly independent of temperature. Subtracting the heats of combustion of the reactants from those of the products the reaction appears to be slightly exothermic, the exact heat evolved differing greatly with the various values accepted for the heats of combustion. A slight error in any of these large quantities makes a large relative error in their difference.

As carried out in the present investigation, the reaction proved to be endothermic. The cooling effect was counter-balanced with the heating coil and it was unnecessary to vaporize carbon tetrachloride in the cooler. Ninety cc. of *N* hydrochloric acid was placed in the thermostat and 10 cc. of methyl acetate was added. Ten cc. of the resulting solution was placed in the calorimeter and 2 cc. samples were withdrawn at intervals from the remaining solution for titration. The course of the reaction was thus followed simultaneously for a period of 3 hours and 42 seconds, by thermal analysis and by chemical analysis. The difference between the titrations at the beginning and end of this period showed that 0.00513 mole of methyl acetate had been hydrolyzed in the calorimeter during this time. To maintain the temperature constant it was necessary to add 5.61 calories from the heating coil. The heat of stirring was 0.405, so that the reaction absorbed a total of 6.015 calories, or 1170 calories per mole.

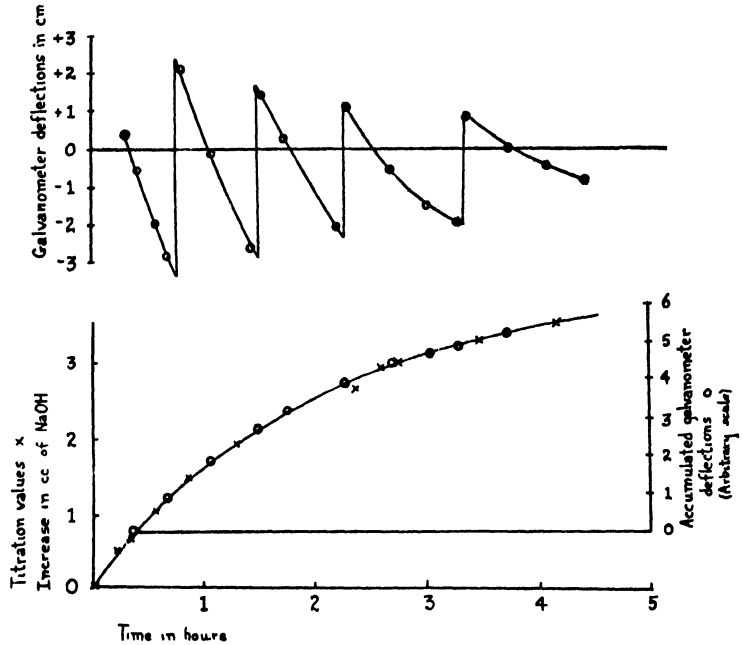

Fig 4. Heat Absorbed in the Hydrolysis of Methyl Acetate

The vertical lines represent measured heat supplied by electric heating coil.

O Titration data. X Calorimetric data

The course of the thermal reaction in a single determination is shown in the upper graph of figure 4, in which the four vertical lines represent the addition of heat—at approximately 0.1 ampere for intervals ranging from 1.5 to 2.5 minutes.

The true hydrolysis reaction is complicated by the presence of the hydrochloric acid, for as the reaction proceeds the reacting substances are removed from the solution and the products are added. Corrections for these heats of mixing were determined experimentally using the vessel shown in figure 3. Five-tenths of 1 cc. or 0.0065 mole of methyl acetate was added to 10 cc. of *N* hydrochloric acid, this quantity representing nearly the amount removed during the reaction in the calorimeter. The heat evolved was 11.45 calories, corresponding to 1763 calories per mole. Check determinations were 1800, 1793, and 1762 giving an average of 1779 calories.

Similarly, when 0.00705 mole of glacial acetic acid, purified by freezing, was added to 10 cc. of *N* hydrochloric acid solution, the heat evolved per mole was respectively 258, 232, 237, and 227, giving an average of 239 calories.

Adding 0.00748 mole of methyl alcohol to 10 cc. *N* hydrochloric acid, the heat of evolution was 1423, 1421, and 1422 calories per mole. The thermal change following the addition of a similar amount of water to *N* hydrochloric acid was negligible.

The summation of the several reactions is then as follows:

Removal of 1 mole methyl acetate from *N* HCl	1779 calories absorbed
Removal of 1 mole water from *N* HCl	0 calories
Addition of 1 mole methyl alcohol to *N* HCl	1422 calories evolved
Addition of 1 mole acetic acid to *N* HCl	239 calories evolved
Total heats of mixing	118 calories absorbed
Total reaction as measured	1170 calories absorbed
Heat of reaction per mole, excluding thermal effects with *N* HCl	1052 calories absorbed

One other direct determination of this reaction is reported in the literature (9), giving an absorption of 1070 calories per mole.

Heat of fermentation of yeast

The growth of yeast is an example of the type of reaction for which this calorimeter is uniquely suited. It is an exothermic reaction which proceeds too slowly for accurate measurement in an ordinary calorimeter. In each experiment three culture tubes of yeast and glucose having identical concentrations were prepared. Two were pasteurized at the time the third was placed in a tube in the calorimeter. At the end of the determination this culture was pasteurized also. All were titrated for glucose content and the difference gave the amount of glucose destroyed during the fermentation.[2]

The fermentation caused the temperature to rise slowly and every hour or so air was passed through the cooler, evaporating carbon tetrachloride and bringing the temperature slightly below the normal value. The course of determination I is shown in figure 5, where the vertical lines represent these periods of cooling.

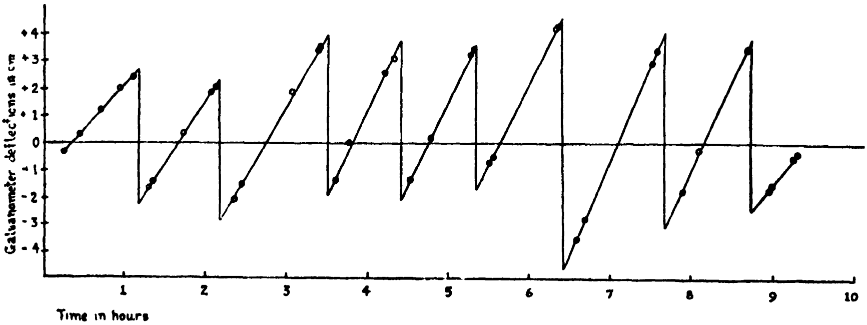

Fig 5 Heat Evolved in the Fermentation of Yeast

The vertical lines represent the measured cooling effect produced by evaporating known quantities of carbon tetrachloride

The heat of fermentation is calculated from the data of determinations I and II as follows:

	I	II	
Weight of carbon tetrachloride	0 4452	0 1777	gram
Heat compensated	21 60	8 64	calories
Time of stirring	9 1	5 5	hours
Heat of stirring	1 10	66	calories
Heat of fermentation	20 50	7 98	calories
Correction for vaporization of water	0 59	23	calories
Corrected heat of fermentation	21 09	8 21	calories
Weight of glucose at beginning	0 260	0 1575	gram
Glucose consumed	0 1617	0 0632	gram
Calories per gram of glucose consumed	130 4	129 9	

The average value of 130.1 calories per gram of glucose is in good agreement with the value 133.3 reported by Rubner (10) using a "microbiocalorimeter" and a Beckmann thermometer.

The correction necessitated by the carrying away of water vapor by the carbon dioxide liberated is calculated from the vapor pressure of water

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[2] The authors are indebted to Dr. P. W. Wilson of the Department of Agricultural Bacteriology for the yeast cultures and their analyses.

(23.7), the volume of the gas, and the heat of vaporization (582 calories per gram).

The reaction of fermentation

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$$

should evolve 147.9 calories per gram of glucose according to data on heats of combustion (11). The fact that the observed value differs from this value by 17.8 calories may be due in part to the heats of solution of glucose and ethyl alcohol in water and in part to the fact that other fermentation reactions are occurring also.

An unsuccessful attempt was made to measure the heat of bacterial growth, but the cultures of *Azotobacter* were not large enough to give a reliable value. Less than 0.2 calorie was evolved during a period of 6 hours.

Thermal studies of the decomposition of nitrogen pentoxide in liquid nitrogen tetroxide will be published later.

SUMMARY

1. An isothermal calorimeter is described, capable of measuring continuously for many hours reactions which evolve less than a calorie an hour

2. Evolution of heat is compensated by evaporating carbon tetrachloride, or other liquid, absorbing the vapor in silica gel, and weighing. Absorption of heat is compensated by measured electrical heating.

3. Special precautions, including the elimination of rubber, are necessary in maintaining an organic liquid in a calorimeter at exactly the same temperature as its surroundings.

4. At 25°C., 48.5 calories was required to offset the vaporization of 1 gram of carbon tetrachloride.

5. Using only 2 cc. of solution, values for the heat of neutralization of 0.5 *N* hydrochloric acid in close agreement with accepted values have been obtained.

6. The hydrolysis of methyl acetate has been found to absorb 1052 calories per mole, after correcting for the heat of mixing with *N* hydrochloric acid.

7. The heat of fermentation of yeast at 25°C. has been found to be 130.1 calories per gram of glucose consumed.

REFERENCES

(1) Keyes and Beattie: J Am Chem. Soc. **46**, 1753 (1924).
(2) Waterman: Phys. Rev. **4**, 161 (1896).
(3) Hirob: J. Faculty Sci. Imp. Univ. Tokyo, Sect. I, **6**, part 4.
(4) Wartenberg and Lerner: Z. physik. Chem **122**, 113 (1926).
(5) Titan: Compt. rend. **178**, 705 (1924).

(6) Berenger-Calvert: J. chim. phys. **24**, 325 (1927).
(7) Richards and Rowe: J. Am. Chem. Soc. **44**, 699 (1922).
(8) Richards and Hall: J. Am. Chem. Soc. **51**, 735 (1929).
(9) Berenger-Calvert: J. chim. **24**, 325 (1927).
(10) Rubner: Arch. Hyg. **57**, 193 (1906).
(11) Wilson and Peterson: Chem. Rev. **8**, 455 (1931).

THE CRITICAL IGNITION OF EXPLOSIVE HYDROGEN MIXTURES

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Thornton (1) observed that the least spark energy required to ignite an explosive mixture of a gas in air varies discontinuously as the composition of the gas is changed continuously. If this condition be represented graphically by plotting the least spark energy for explosion of mixtures with the proportion of explosive gas in air, the resulting ignition curve is composed of a series of distinct "steps." This phenomenon, which is called "stepped" or "critical" ignition, is shown to depend upon the presence of nitrogen in the gas mixtures considered here.

It was found that the ignition curve for hydrogen in air mixtures has two very distinct steps. On the other hand, smooth curves were found for mixtures of hydrogen and oxygen and also for mixtures of hydrogen, argon and oxygen wherein the argon was present in the same proportion as nitrogen in the air mixtures. The purpose of substituting argon for nitrogen was to determine if the action of nitrogen on ignition differed from that of an inert gas, and this seems to be the case.

EXPERIMENTAL

The explosions were carried out in an iron bomb of about 100 cc. capacity with a spark gap consisting of a steel needle cathode and a plane anode also of steel. This bomb was conveniently made of ordinary pipe fitting, the main piece a one and one-fourth inch cross. Two one-half inch holes in the cross on opposite sides of the spark gap were fitted with rubber stoppers to provide a safe outlet for the exploding gas, which blows the stoppers out. Steel phonograph needles were used for the cathode. These were replaced for each explosion.

The gas mixtures were made up in volumes of three liters by displacement of water from the gas container. The measurements were made on gases saturated with water vapor and at room temperature. The bomb is filled with gas by mercury displacement.

The electrical arrangement for discharging the spark in the gas consists of charging condensers from a source of direct current with the electrodes wide apart. The direct current source is then disconnected and the condensers discharged by approaching the electrodes. Not more than three seconds need elapse between the time the direct current connection is broken and the time the electrodes are brought within sparking distance.

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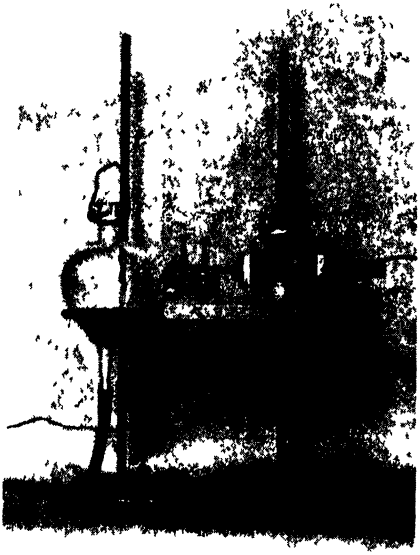

FIG. 1 EXPLOSION BOMB

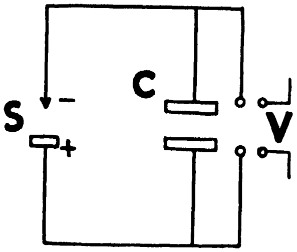

FIG. 2. WIRING DIAGRAM

S, spark gap; C, condenser; V, voltage of D. C. source

During this interval of time there is some leakage loss in the condensers, but it has been found that this loss is negligible up to about twenty seconds.

The energy "E" expressed in terms of the capacity and voltage of the condensers discharged in the spark is expressed as follows:

$$E = 1/2\ CV^2$$

The curves in figure 3 are for ignition at 160 volts, spark potential. Similar curves have been obtained for the ignition of the same hydrogen mixtures at 100 volts, but the least spark energy at this potential is higher than the least spark energy for ignition at 160 volts.

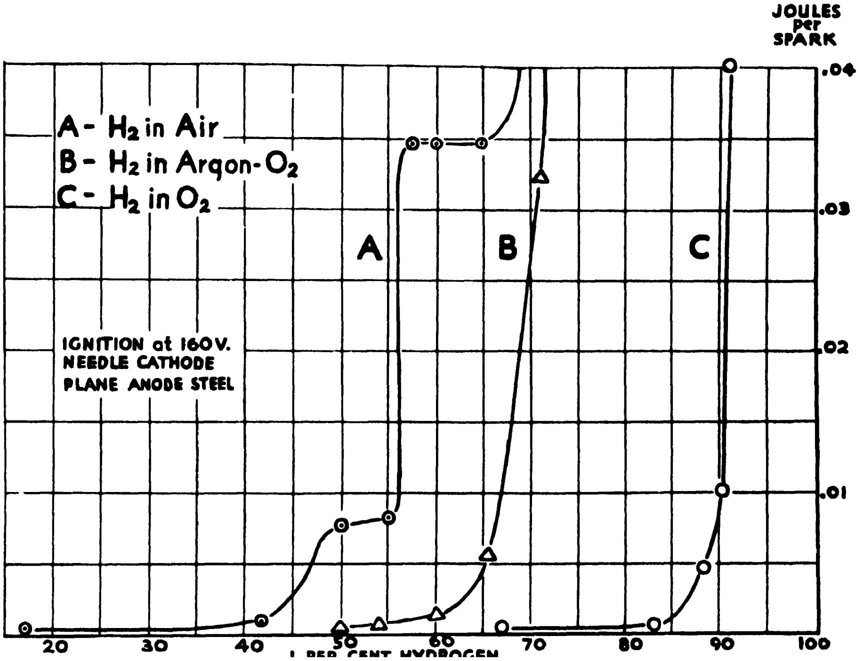

FIG. 3. IGNITION CURVES FOR IGNITION OF HYDROGEN MIXTURES

REFERENCE

(1) THORNTON: Proc. Roy. Soc. London **91**, 17 (1914). The Ignition of Gases by Condenser Discharge Sparks.

APPLICATION OF BLAIR-LEIGHTON EQUATION TO X-RAYS

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Blair and Leighton (1) have presented an equation,

$$\frac{dx}{dt} = K_1x^{\frac{1}{2}}\,(b - x) - K_2x$$

for the time rate of growth of the latent photographic image, when a photographic emulsion was exposed to a blue light of constant intensity. In this equation, x is the developable density existing at any time t; b is the ideal maximum developable density (defined below); and K_1 and K_2 are reaction velocity constants of forward and reverse photographic reactions. In this paper an attempt will be made to show that this equation also holds for the rate of formation of the latent photographic image when produced by x-rays of constant intensity.

METHOD OF PROCEDURE

Ordinary x-ray plates were not used because of their relative opacity, but instead glass plates coated with regular lantern slide emulsion. For ease and greater accuracy in determining the density, this coating was made about one-third as thick as the ordinary lantern slide emulsion. The source of x-rays was a deep therapy machine. These x-rays were filtered through 1 mm. of aluminum to render them more homogeneous. The conditions during exposure were kept constant by keeping the current through the tube and the operating line potential constant. Under these conditions the intensity of the x-rays was found to be uniform and constant, by means of a dosimeter.

After coating, the plates were dried in an inclined position, making the emulsion slightly thicker on the lower end than the upper. To reduce the error which this would produce, the plates were cut into two longitudinal halves, one of which was turned end for end before exposure. Then exposures of increasing times were given to consecutive portions of the same plate. Several plates were necessary to obtain all the points shown on figure 1. The maximum exposure on one plate was repeated as the minimum exposure on the next. The plates were then developed in a ferrous oxalate developer described by Hurter and Driffield (2) for 20 minutes at 19°C. They were then fixed for 6 minutes in acid sodium thiosulfate solution, and washed and dried in the usual manner. The resultant densities were measured in the same manner as that described by Blair and Leighton (1). The densities of corresponding portions on each half plate receiving the same exposure were measured and averaged.

As the separate plates had emulsions of slightly different average thicknesses, the plotted densities would not form a continuous curve. In several cases there would be slight breaks between the series of data obtained from one plate and that obtained from the next one. The overlapping of times of exposure made it possible to express the densities of all the plates in terms of any one chosen as standard by the use of a small multiplying factor. This factor was the ratio between the average density of one portion of a plate and the average density of a corresponding portion of another, each having received the same exposure. The densities produced by exposures to x-rays are shown by the circles in figure 1.

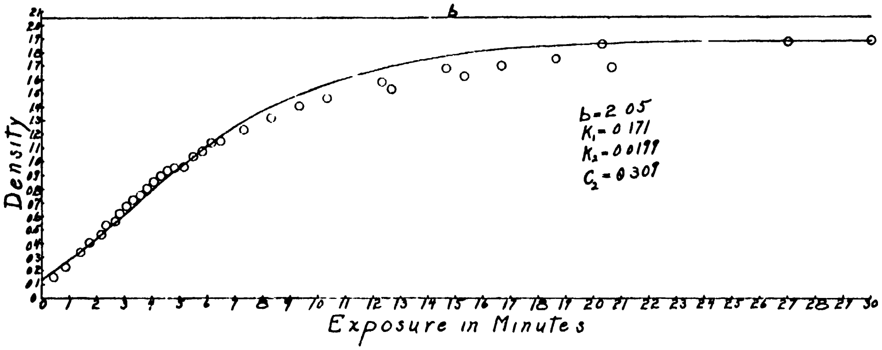

FIG. 1. THE DENSITIES PRODUCED BY EXPOSURE TO X-RAYS AND THE DENSITIES INDICATED BY THE BLAIR-LEIGHTON EQUATION

DETERMINATION OF *b*

The quantity, *b*, mentioned in the above equation is the ideal maximum developable density. It may be briefly defined as that density the plate would have if every grain of silver halide were developed. Blair and Leighton (1) have presented a chemical means of determining this quantity. It may also be determined in a much easier, but sufficiently accurate manner. Jones and Hall (3) have shown that increasing maximum developable densities are obtained by exposures to increasing intensities of light. They showed, using the terminology of Blair and Leighton, that when a plate was exposed to intense light, the maximum attainable density approached the ideal maximum developable density. On the basis of their work, one-half of a plate was exposed for the optimum time to the concentrated beam of a carbon arc projection lantern. The other half was exposed for 30 minutes to x-rays to produce the maximum attainable density from this source. The maximum attainable density, shown by the highest point on figure 1, was multiplied by the ratio of the developable density produced by the arc on one half of the plate, to that produced by the x-rays on the other half. This gave a close approximation to the ideal maximum developable density in terms of the plate chosen as standard. This quantity is shown by the straight line in figure 1.

INTEGRATION OF EQUATION

If, in the equation,

$$\frac{dx}{dt} = K_1 x^{\frac{1}{2}} (b - x) - K_2 x$$

we let $x^{\frac{1}{2}} = z$ and add and subtract the quantity $\frac{K_2^2}{4K_1^2}$ the equation may be put in the standard form of integration,

$$\frac{2dz}{K_1 \left[b + \frac{K_2^2}{4K_1^2} - \left(z + \frac{K_2}{2K_1} \right)^2 \right]} = dt$$

There are several integrals of this equation. In the paper by Blair and Leighton (1) it was integrated into a logarithmic form. It may, however, be integrated into the following form

$$\frac{2}{K_1 \sqrt{b + \frac{K_2^2}{4K_1^2}}} \tanh^{-1} \left(\frac{z + \frac{K_2}{2K_1}}{\sqrt{b + \frac{K_2^2}{4K_1^2}}} \right) = t + C_1$$

where C_1 is a constant of integration. Substituting $x^{\frac{1}{2}}$ for z and solving for x we obtain

$$x = \left[\sqrt{b + \frac{K_2^2}{4K_1^2}} \tanh \left(\frac{K_1}{2} \sqrt{b + \frac{K_2^2}{4K_1^2}}\, t + C_2 \right) - \frac{K_2}{2K_1} \right]^2 \qquad (1)$$

where

$$C_2 = \frac{K_1 C_1}{2} \sqrt{b + \frac{K_2^2}{4K_1^2}}$$

EVALUATION OF CONSTANTS

From the data shown in figure 1 a ratio between K_1 and K_2 was determined where the slope is 0. Then K_1 and K_2 were evaluated by graphical means from the experimental curve by measuring the slope at some value of x. The constant C_2 was then found by taking the x and t coördinates of some point on the experimental curve. The curve in figure 1 shows the values of x for the times t given by equation 1.

SUMMARY

A different method of evaluating the ideal maximum developable density is described, and a different integral of the Blair-Leighton equation is presented. Evidence is presented that this equation also expresses the rate of formation of the latent photographic image by x-rays.

REFERENCES

(1) Blair and Leighton: J. Phys. Chem. **36**, 1649 (1932).
(2) Hurter and Driffield: Phot. J. **38**, 76 (1898).
(3) Jones and Hall: Proc. 7th Intern. Congr. Phot., p. 115 (1929).

SOLID POLYIODIDES OF CESIUM

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It has recently been shown conclusively by Briggs, Greenawald, and Leonard (1) and by Briggs (2) that cesium iodide and iodine form two binary addition products having the formulas CsI_3 and CsI_4 and that the compound CsI_5 does not exist, at least above 25°C. Water solutions were used by these investigators in preparing the compounds at 25°C., but as the latter were anhydrous, they are undoubtedly the only stable binary compounds which can form at 25°C., independent of what solvent is used, or indeed of whether any solvent is used. On the other hand, Abegg and Hamburger (3) working on the system cesium iodide–iodine–benzene showed from solubility results that there was evidence of a higher polyiodide which they believed to be CsI_9. They made no attempt to determine whether a solvated ternary compound existed. Since it has recently been shown (4) that potassium iodide forms such a ternary compound with benzene we have investigated the system cesium iodide–iodine–benzene at 6°C. and at 25°C. and also the system containing toluene in place of benzene.

The cesium iodide used was an exceedingly pure sample which had been prepared by heating the higher polyiodide. The latter had been prepared by crystallization from water containing an excess of iodine. Benzene, toluene, and iodine were prepared by the methods described previously by Foote and Bradley (4). The apparatus and methods are also fully described in the same paper.

THE SYSTEM TOLUENE–CESIUM IODIDE–IODINE

In this system, qualitative tests showed that no solvated compounds were formed and that cesium iodide, like potassium iodide, is insoluble in the solvent. The investigation was therefore relatively simple. The original components were accurately weighed and by determining iodine in the solution after equilibrium had been reached, the composition of the solid residues, whether mixtures or pure compounds, could be calculated with probably greater accuracy than could be obtained by direct analysis. The results obtained are given in table 1.

The results show clearly at each temperature that there are three univariant points. At each, the solubility is constant and the residues consist of a variable mixture of two solids; the two pure compounds, which are in equilibrium with solutions of varying composition, exist between the univariant points. The average of the six results obtained for free iodine in CsI_4 is 59.35; and of the four results for CsI_3 is 49.73. The corresponding calculated percentages are 59.44 and 49.42. The results confirm those of Briggs and his coworkers (1) at 25°C., using water as the solvent, and show that the same compounds also exist at 6°C. No solvated ternary compound with toluene exists.

TABLE 1

The system toluene-cesium iodide-iodine

$T = 25°C$			$T = 6°C$		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0 060	16 66	CsI and CsI_3	0 024	11 18	CsI and CsI_3
0 047	48 18	CsI and CsI_3	0 024	46 00	CsI and CsI_3
0 77	50 13	CsI_3	0 54	49 70	CsI_3
1 72	49 57	CsI_3	1 08	49 50	CsI_3
2 53	51 42	CsI_3 and CsI_4	1 53	52 30	CsI_3 and CsI_4
2 54	53 80	CsI_3 and CsI_4	1 53	56 25	CsI_3 and CsI_4
2 54	57 21	CsI_3 and CsI_4			
			4 35	59 76	CsI_4
3 09	59 25	CsI_4	6 74	59 79	CsI_4
9 90	58 53	CsI_4			
13 45	59 17	CsI_4			
14 66	59 58	CsI_4	10 39	64 06	CsI_4 and I_2
			10 43	89 77	CsI_4 and I_2
15 46	62 24	CsI_4 and I_2			
15 37	94 32	CsI_4 and I_2			

THE SYSTEM BENZENE-CESIUM IODIDE-IODINE

Qualitative tests showed that at the iodine end of the system the solids contained benzene, showing the existence of a ternary compound. The simple method of calculating the composition of the residue which was adopted with toluene therefore could not be used in this case and it was necessary to analyze the residues, at least when the pure solvated compound was present. The Schreinemaker method of determining the composition of the solids by the analysis of the wet residues was entirely unsuitable in this case on account of the position and form of the solubility curve. We were therefore forced to determine the composition of the compound by

TABLE 2

The system benzene–cesium iodide–iodine

NO	IODINE IN SOLUTION	SOLID RESIDUE			RESIDUE CONTAINS
		Iodine	Cesium iodide	Benzene	
			T = 25°C.		
	per cent	*per cent*	*per cent*	*per cent*	
1	0 049	10 00	90 00	none*	CsI and CsI_3
2	0 045	42 14	57 86	none*	CsI and CsI_3
3	0 77	49 38	50 62	none*	CsI_3
4	1 34	50 00	50 00	none*	CsI_3
5	2 35	53 15	46 85	none*	CsI_3 and CsI_4
6	2 34	56 68	43 32	none*	CsI_3 and CsI_4
7	3 89	59 40	40 60	none*	CsI_4
8	5 27	59 40	40 60	none*	CsI_4
9	7 76	58 6	33 3	8 1†	CsI_4 and T. C.§
10	7 74	66 2	14 7	9 1†	CsI_4 and T. C.§
11	8 88	75 54	15 96	8 50‡	T. C §
12	12 19	73 23	16 22	10 55‡	T. C.§
13	14 09	79 9	12 5	7 6†	T. C § and I_2
14	13 83	91 8	5 1	3 1†	T. C § and I_2
			T = 6°C.		
15	0 022	12 07	87 93	none*	CsI and CsI_3
16	0 024	47 42	52 58	none*	CsI and CsI_3
17	0 55	49 25	50 75	none*	CsI_3
18	1 20	49 41	50 59	none*	CsI_3
19	1 31	53 98	46 02	none*	CsI_3 and CsI_4
20	1 30	56 85	43 15	none*	CsI_3 and CsI_4
21	2 00	59 37	40 63	none*	CsI_4
22	3 41	59 16	40 84	none*	CsI_4
23	3 80	59 8	39 9	0 3†	CsI_4 and T. C.§
24	3 80	67 3	27 1	5 6†	CsI_4 and T. C.§
25	3 81	71 31	20 15	8 54†	CsI_4 and T. C.§
26	4 55	74 22	16 74	9 04‡	T. C.§
27	6 25	75 23	15 23	9 54‡	T. C.§
28	6 60	76 33	15 64	8 03‡	T. C.§
29	8 59	81 2	11 7	7 1†	T. C. and I_2
30	8 58	92 3	4 8	2 9†	T. C. and I_2

* Composition of the solid calculated as in the toluene system. Residue unsolvated.

† Composition of the solid obtained graphically.

‡ Composition of the solid determined by analysis (benzene by difference).

§ Ternary compound.

analysis, after removing it from the solution and freeing it from the mother liquor by pressing rapidly between filter papers. The compound loses its benzene rapidly on standing. On the other hand, the color changes appreciably as it decomposes, so that it was not difficult to determine rather closely from the appearance when the mother liquor was removed. In analyzing the compound, free iodine was determined by titration with thiosulfate and cesium iodide by heating to remove free iodine and benzene. The latter was determined by difference. The composition of the residues at the univariant points could be determined graphically with sufficient accuracy when the composition of the solvated compound was known.

The results given in table 2 were obtained. The method used in determining the composition of the residues is indicated in each case.

The data in table 2 show in an entirely satisfactory manner the existence of the two compounds CsI_3 and CsI_4 at both 6°C. and 25°C. Besides these two compounds, however, there is a third solvated compound. It was present in pure condition, as shown by the solubility results, in Nos. 11 to 12 at 25°C. and in Nos. 26 to 28 at 6°C. The ratio $CsI:I:C_6H_6$ has been calculated for each of these residues, and the results are given in table 3.

TABLE 3

Showing the ratio $CsI:I:C_6H_6$ *for each of the five residues in which the pure ternary compound was present. The ratios are calculated from the analytical data in table 2*

NO.	RATIO		
	CsI	I :	C_6H_6
11	1 0	9 64	1.77
12	1 0	9 24	2 16
26	1 0	9 07	1.79
27	1 0	10 10	2.08
28	1 0	9 99	1 71
Average =	1 0	9 52	1 90

In considering these ratios, it must be borne in mind that the material used in the analysis was very finely divided, and was of necessity contaminated with iodine from the solution, since the benzene in the latter was exceedingly volatile and deposited iodine as it evaporated. The ratio $CsI:C_6H_6$ appears to be definitely 1:2, and allowing for the fact that the analytical results should be high in iodine, the ratio CsI:I is nearly 1:9, so that the most probable formula, based on the above analyses, is $CsI_{10}\cdot 2C_6H_6$, in which the ratio CsI:I is less certain than the ratio $CsI:C_6H_6$.

It is evident, however, that the ratio CsI:I can be calculated just as in the unsolvated residues, provided the ratio of $CsI:C_6H_6$ in the residue is known. Judging from the results on the unsolvated residues, this method should give more reliable results than direct analyses. In table 4 we give the charges used, the calculated composition of the residue assuming the ratio $CsI:C_6H_6 = 1:2$, and the ratio CsI:I calculated from the composition of the residues.

The ratio I/CsI is nearly 9, and the formula is therefore $CsI_{10} \cdot 2C_6H_6$ or $2CsI \cdot 9I_2 \cdot 4C_6H_6$. The writers are not unaware that this formula is most unusual and *a priori* highly improbable. The composition as determined by analysis, and as calculated in table 4, however, seems to exclude any simpler ratio. The corresponding ternary compound of potassium has the formula $KI_9 \cdot 3C_6H_6$ and is therefore of different type, the only evident relationship being that the cesium compound may be derived from the potassium by the substitution of one atom of iodine for one molecule of benzene.

TABLE 4

Showing the weight of each component in the original mixtures; the calculated per cent of cesium iodide and of iodine in the residues, assuming the ratio $CsI:C_6H_6 = 1.2$; *and the molecular ratio* I:CsI *in the residues*

NO	CESIUM IODIDE	IODINE	BENZENE	CALCULATED CsI IN RESIDUE	CALCULATED I_2 IN RESIDUE	RATIO $\frac{I}{CsI}$
	grams	*grams*	*grams*	*per cent*	*per cent*	
11	0 67	6 12	30 833	15 85	74 62	9 63
12	0 67	7 02	30 795	17 30	72 30	8 55
26	1 22	6 70	30 134	16 82	73 06	8 89
27	1 22	7 168	30 488	17 09	72 62	8 70
28	1 22	7 637	29 917	16 20	74 05	9 35

Average = 9 02

At any univariant point in the systems investigated two solids are present, and their dissociation pressure of iodine is equal to the partial pressure of iodine in the solution. The latter is closely proportional to the molar fraction of iodine in solution, as all the solutions are dilute. The dissociation pressure of any polyiodide compared with pure iodine (or the activity) is therefore given very closely by the expression $\frac{C}{C_0}$ in which C is the molar concentration of iodine in solution at a univariant point, and C_0 is the corresponding value for pure iodine. The latter is practically identical with that at the univariant point where iodine is one of the solid phases, as cesium iodide is insoluble.

In table 5, the necessary data and the values of the ratio $\frac{C}{C_0}$ are given at 25°C. and at 6°C. for both the benzene and the toluene solutions, so far as the data are comparable. The data for the point in the benzene system in which the solids consist of CsI_4 and the ternary compound have been omitted, as there is no comparable point for toluene.

The differences between comparable values of $\frac{C}{C_0}$ for the benzene and toluene systems is of the same order as the error in determining the composition of the solutions. Assuming the vapor pressures of iodine at 6°C. and 25°C. are 0.0546 mm. and 0.313 mm.,[1] and the values of $\frac{C}{C_0}$ in table 5, the dissociation pressures of CsI_4 at 6°C. and 25°C. are respectively 0.00775 mm. and 0.0479 mm. For CsI_3, the values are 0.000131 and 0.000970 mm.

TABLE 5

Values of the ratio C/C_0 at 25°C. and at 6°C.

SOLIDS PRESENT	WEIGHT PER CENT OF IODINE IN SOLUTION	MOLE PER CENT OF IODINE IN SOLUTION	$\frac{C}{C_0}$
	Benzene. T = 25°C.		
I_2 and T. C.	13 96	4 75 (C_0)	
CsI_4 and CsI_3	2 35	0 73	0 155
CsI_3 and CsI	0 047	0 014	0 0030
	Toluene T = 25°C.		
I_2 and CsI_4	15 42	6 20 (C_0)	
CsI_4 and CsI_3	2 54	0 94	0 151
CsI_3 and CsI	0 054	0 020	0 0032
	Benzene. T = 6°C.		
I_2 and T. C.	8 59	2 81 (C_0)	
CsI_4 and CsI_3	1 31	0 41	0 145
CsI_3 and CsI	0 023	0 0071	0 0025
	Toluene. T = 6°C.		
I_2 and CsI_4	10 41	4 04 (C_0)	
CsI_4 and CsI_3	1 53	0 56	0 139
CsI_3 and CsI	0 024	0 0087	0 0022

From these values, the heats of dissociation of CsI_4 and CsI_3, calculated by van't Hoff's equation, are found to be respectively −15,800 and −17,500 calories. These values, as well as those for the dissociation pressures, are based on the solubility data. Since some of the solubilities are very low, the relative error in them causes a considerable error in these calculations. This error appears to be less than ±5 per cent.

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[1] By interpolation from the data given in the International Critical Tables.

SUMMARY

The systems cesium iodide–iodine–benzene and cesium iodide–iodine–toluene have been investigated at 6°C. and at 25°C. With toluene, no ternary compound exists, and the two binary compounds found were CsI_3 and CsI_4, confirming the results of Briggs and his coworkers at 25°C. With benzene, in addition to the two binary compounds, there is also a ternary compound.

The results on the dissociation pressures of the binary compounds show close agreement when calculated from the data on the benzene and on the toluene systems.

REFERENCES

(1) Briggs, Greenawald, and Leonard: J. Phys. Chem. **34**, 1951 (1930).
(2) Briggs: J. Phys Chem. **34**, 2260 (1930).
(3) Abegg and Hamburger: Z. anorg. Chem. **50**, 403 (1906).
(4) Foote and Bradley: J. Phys. Chem. **36**, 673 (1932).

THE SOLID POLYIODIDE OF AMMONIUM

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It has been shown by Abegg and Hamburger (1), by investigating systems of the type alkali iodide-iodine-benzene, that a number of solid polyiodides exist, but the fact was overlooked that some of the compounds formed were in reality ternary compounds containing benzene. Such ternary compounds form with potassium iodide (2) and with cesium iodide (see preceding article). We give below the results obtained with ammonium iodide and iodine at two temperatures, using as solvents benzene and toluene. Unlike the potassium and cesium compounds, it has been found that ammonium forms only the binary triiodide.

The method of investigation has been described previously (3). Qualitative tests on the solid residues showed the absence of either benzene or toluene. It was therefore possible, starting with weighed amounts of each component and analyzing the solutions, to calculate the composition of the residues with entirely satisfactory accuracy. Ammonium iodide is practically insoluble in both the toluene and benzene solutions, so that it was only necessary to determine iodine. The results obtained are given in tables 1 and 2.

The data in these two tables show that ammonium triiodide is the only

TABLE 1

The system benzene–ammonium iodide-iodine

$T = 25$°C			$T = 6$°C		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0.77	10.00	NH_4I and NH_4I_3	0.39	10.49	NH_4I and NH_4I_3
0.80	39.91	NH_4I and NH_4I_3	0.42	55.18	NH_4I and NH_4I_3
0.79	59.35	NH_4I and NH_4I_3			
5.60	64.17	NH_4I_3	3.45	63.90	NH_4I_3
10.34	64.33	NH_4I_3	5.77	63.96	NH_4I_3
13.94	94.96	NH_4I_3 and I_2	8.52	70.13	NH_4I_3 and I_2
			8.58	94.99	NH_4I_3 and I_2

polyiodide which forms, and that it is stable over a wide range of iodine concentrations.

TABLE 2

The system toluene–ammonium iodide–iodine

T = 25°C.			T = 6°C		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0 88	9 87	NH_4I and NH_4I_3	0 46	12 39	NH_4I and NH_4I_3
0 88	47 45	NH_4I and NH_4I_3	0 47	59 08	NH_4I and NH_4I_3
0 89	55 93	NH_4I and NH_4I_3			
5 84	63 95	NH_4I_3	2 92	63 88	NH_4I_3
10 85	63 93	NH_4I_3	5 36	63 95	NH_4I_3
15 75	68 14	NH_4I_3 and I_2	10 24	67 80	NH_4I_3 and I_2
15 75	86 09	NH_4I_3 and I_2	10 19	94 65	NH_4I_3 and I_2
15 91	94 88	NH_4I_3 and I_2			

The average of the eight results on available iodine in the residues consisting of the pure compound is 64.01 per cent. The calculated value for NH_4I_3 is 63.65 per cent of available iodine.

TABLE 3

The average percentage by weight of iodine in solution at each univariant point, the corresponding molecular percentages of iodine, C and C_0, and their ratio

SOLVENT	SOLIDS PRESENT	PER CENT OF IODINE IN SOLUTION	MOLECULAR PER CENT OF IODINE IN SOLUTION	$\frac{C}{C_0}$
		T = 25°C.		
Benzene	I_2 and NH_4I_3	13 94	4 75 (C_0)	
Benzene	NH_4I_3 and NH_4I	0 79	0 24 (C)	0 0515
Toluene.	I_2 and NH_4I_3	15 80	6 37 (C_0)	
Toluene	NH_4I_3 and NH_4I	0 88	0 32 (C)	0 0504
		T = 6°C.		
Benzene	I_2 and NH_4I_3	8 55	2 80 (C_0)	
Benzene	NH_4I_3 and NH_4I	0 41	0 13 (C)	0 0452
Toluene..	I_2 and NH_4I_3	10 22	3 97 (C_0)	
Toluene...	NH_4I_3 and NH_4I	0 47	0 17 (C)	0 0431

Taking the average values of $\frac{C}{C_0}$ at each temperature, and the vapor pressure of iodine given in the preceding article, the calculated dissociation pressures of ammonium triiodide at 25°C. and at 6°C. are 0.0160 mm. and 0.00241 mm., respectively.

As pointed out in the preceding article on cesium polyiodides, the activity of the triiodide compared with pure iodine is given rather accurately by the ratio of molar concentrations of iodine at the two univariant points. In table 3, we give the average percentage by weight of iodine found in solution at the univariant points, the corresponding molecular percentages of iodine, and their ratio. The differences between the values of $\frac{C}{C_0}$ for the benzene and toluene solutions, at each temperature, are of the same order as the error in determining the iodine concentrations.

As ammonium triiodide can be prepared readily in very pure condition and is the only binary periodide of ammonium, it seems worth while to point out that it furnishes a very convenient way of maintaining a constant, low concentration of iodine vapor which can be varied at will by variation in temperature. Its behavior in this respect is similar to that of a hydrated salt in maintaining a constant humidity.

SUMMARY

Solubility results on mixtures of ammonium iodide and iodine in benzene and in toluene show that the compound NH_4I_3 is the only binary periodide which forms above 6°C. No solvated compound with benzene or toluene exists. The behavior of ammonium iodide is entirely unlike that of potassium iodide, which forms no binary periodide but does form a ternary solvated compound.

The results on the dissociation pressure of the triiodide at each temperature show close agreement when calculated from the data on the benzene and on the toluene systems.

REFERENCES

(1) ABEGG AND HAMBURGER: Z. anorg. Chem. **50**, 403 (1906).
(2) GRACE, N. S.: J. Chem Soc. **1931**, 594.
FOOTE, H. W., AND BRADLEY, W. M.: J. Phys. Chem. **36**, 673 (1932).
(3) FOOTE, H. W., BRADLEY, W. M., AND FLEISCHER, MICHAEL: J. Phys. Chem. **37**, 21 (1933).

AN IMPROVED METHOD FOR THE DETERMINATION OF ISOTHERMALS BY THE RETENTIVITY TECHNIQUE

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INTRODUCTION

In a previous publication (1) a new method for the determination of sorption isothermals of vapors on charcoal was described; the present paper records a development of this method whereby the accuracy is greatly increased and the technique simplified. No experimental details are given, as these were described fully in the previous papers (1, 2).

This method consisted in the conversion of the approximate isothermals obtained under the retentivity test conditions into true isothermals. Briefly, this was achieved by carrying out a number of determinations employing columns of charcoal of different lengths and plotting the logarithm of the weight of vapor retained against the logarithm of the volume of charcoal for a constant volume of air passed, and then extrapolating the weight figures to 1 cc. to get rid of the "pressure-length effect." The tangents drawn to the retentivity curve obtained from these extrapolated data gave rise to the true isothermal.

At the time of publication it was realized that this method would not apply to an isothermal of the water type on or above that portion where the quantity of substance sorbed increases rapidly for a small increase of pressure, and an attempt was made to make it hold good under all conditions. As this technique seemed to allow of an extremely detailed examination being made of the structure of the isothermal, an experiment was carried out on a single column of charcoal of about 10 cc. volume, charged with water vapor, the flow of air being interrupted at very frequent intervals. By this means it was hoped to anchor the retentivity curve exactly over its entire range, and then by drawing an extremely large number of tangents, the detailed isothermal structure would be obtained.

The result of this experiment was characterized by one very striking fact; the retentivity curve was found to consist of a series of straight lines intersecting one another at definite points (e.g., figure 1, which represents the retentivity curve of a water isothermal on Charcoal K 2 at 15°C. Charcoal K2 was a peat charcoal activated with phosphoric acid; apparent density = 0.312). The resultant isothermal (figure 2, dotted lines) does not consist of a series of rounded loops as had been obtained heretofore; the breaks are all sharply rectangular. It was found that with isothermals on silica gel, as had been previously discovered in the case of charcoal, there are no breaks below 0.1 mm., the isothermal consisting of a smooth curve (3). This rectangular structure makes it possible for an improved method for the determination of adsorption isothermals to be put forward which will hold good under all conditions using but a single column of charcoal.

If one charges the charcoal column at a vapor pressure which is intermediate between two horizontal portions of the isothermal, then on desorption a linear section will result on the retentivity curve, and at a definite quantity value this line will be intersected by another. Now the straight lines correspond to constant pressures over the quantity ranges indicated and will give rise to two horizontal sections on the isothermal. Only the second of these corresponds to a true step, however, for the first is inherent in the experimental procedure, since it is caused by the formation of the gradient inside the column. Reference to a previous publication (1) will show clearly how this occurs. Owing to this gradient the average quantity of vapor in the column expressed as milligrams per gram is smaller than corresponds to the pressure over the end of the column. The error which this gradient introduces in the quantity value steadily diminishes until at a very small quantity figure it is zero, the average quantity in the column and the quantity corresponding to the pressure over the end of the column being identical.

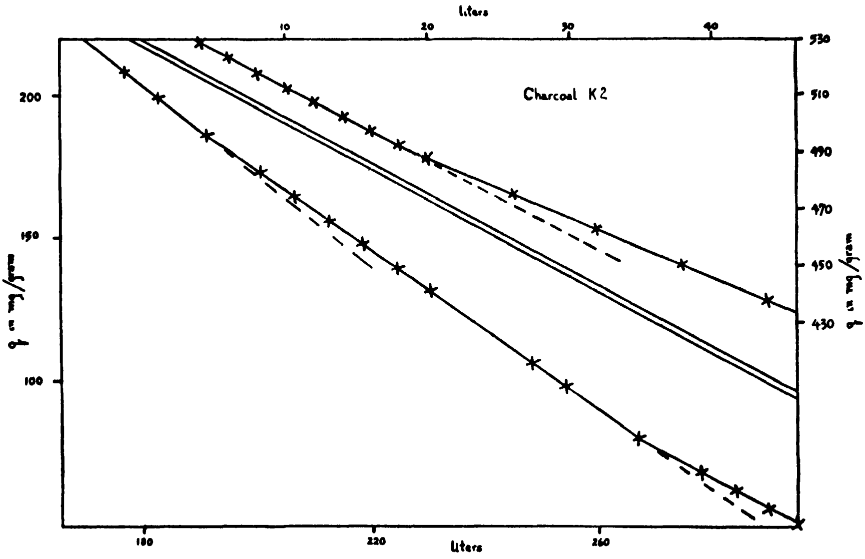

FIG. 1

The improved technique is essentially as follows:

(a) The pressure is calculated from the slope of the linear sections of the retentivity curve, the difference in the quantity values giving the amount of substance which has been carried away in a certain volume of air (the difference of the corresponding volume figures).

(b) The quantity values are calculated thus: The amount of substance held at zero pressure is subtracted from the quantity figures for all retentivity curve breaks. These are "corrected" quantity values. The ratio of the corrected saturation figure to the corrected quantity figure at the first retentivity break is calculated. The corrected quantity values for each break are then multiplied by this ratio and the amount held at zero pressure added, whereby the true quantity for each break is obtained, resulting in a true isothermal.

TABLE 1

(1)	(2)	(3)	(4)
542 8	519 2	—	—
488 0	464 4	519 2	542 8
390 3	366 7	410 1	433 7
284 5	260 9	291 8	315 4
186 1	162 5	181 7	205 3
80 4	56 8	63 5	87 1
35 7	12 1	13 5	37 1
29 0	5 4	6 0	29 6
26 3	2 7	3 0	26 6
23 6	0 0	0 0	23 6

A criticism may be advanced in the case where the initial charging pressure coincided with that at which a step occurred, in which case it would appear that the linear section on the retentivity curve due to the formation of the gradient and that due to the first step would be continuous, thus preventing a calculation of the true isothermal. It has been shown, however, by sorbing from an air stream charged to a definite pressure with vapor, that one must charge at a distinctly higher pressure value to pass along the horizontal portion of a step. This being so it is perfectly valid to use this new method, since the sorption point will not pass along the horizontal step but will remain on the vertical portion joining this step with the one below.

In table 1 the method of operation is shown in full. The vertical columns have the following significance: (1) quantity values at the retentivity curve breaks; (2) the corrected quantity figures; (3) the figures in the previous column multiplied by the ratio of the corrected saturation figure to the corrected quantity figure at the first retentivity break; (4) the latter column + the amount held at zero pressure, all figures being expressed as milligrams per gram. The quantity held at zero pressure is 23.6 mg. per gram.

The isothermal in figure 2 has been converted to a true isothermal (continuous lines) in this manner, the individual points being omitted. The figures for the pressure and quantity range of each step and the number of experimental points on that step are given in table 2.

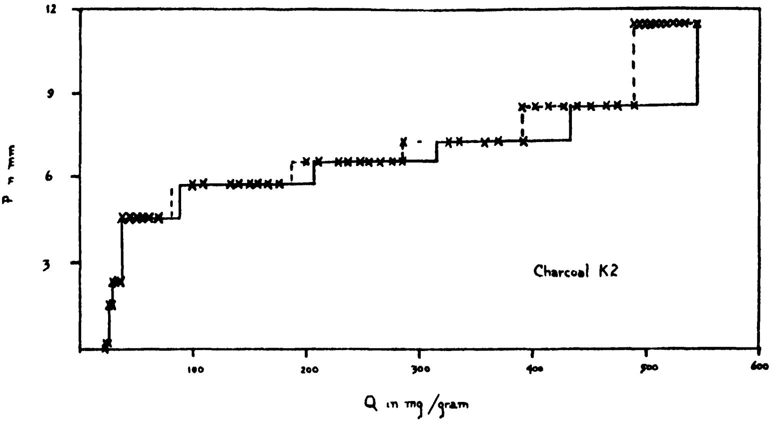

FIG 2

TABLE 2

PRESSURE OF BREAK	QUANTITY RANGE OF STEP	DIFFERENCE	NUMBER OF EXPERIMENTAL POINTS
› ım	mg / gram	mg / gram	
11 53	—	—	10
8 60	542 8–433 7	109 1	8
7 35	433 7–315 4	118 3	6
6 61	315 4–205 3	110 1	9
5 80	205 3– 87 1	118 2	8
4 58	87 1– 37 1	50 0	6
2 35	37 1– 29 6	7 5	5
1 55	29 6– 26 6	3 0	4
0 25	26 6– 23 6	3 0	3

EXPERIMENTAL

Desorption experiments in an air stream charged with vapor at definite pressures

To verify the rectangular structure of adsorption isothermals and also to justify this new procedure, desorption experiments were carried out using an air stream charged to definite pressures with vapor, the points obtained being checked against the isothermals obtained by the improved retentivity method. Such experiments have been carried out with water and carbon tetrachloride on charcoal and on silica gel.

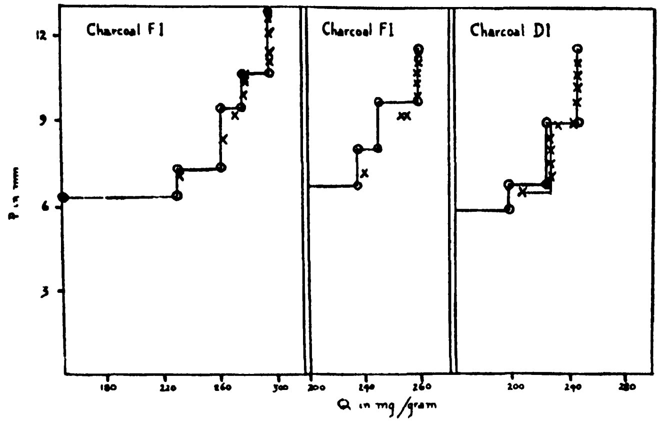

FIG. 3

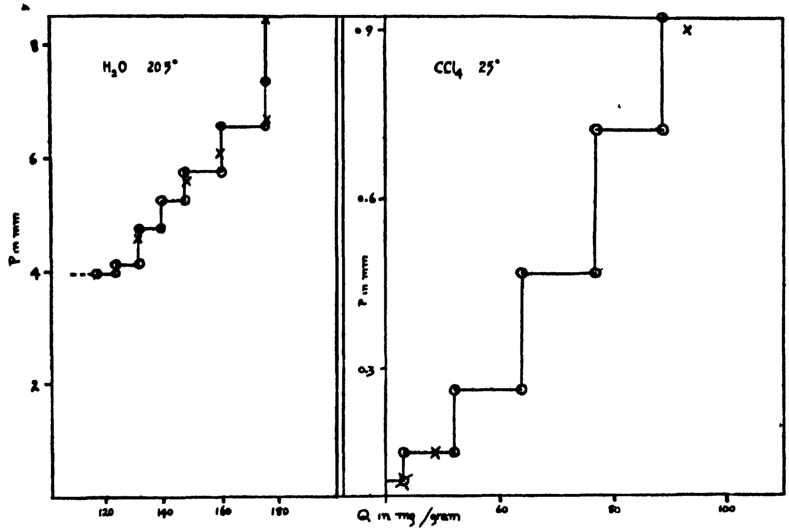

FIG. 4

The crosses represent such desorption points and the circles mark the ends of the steps (the individual points being omitted) in the isothermals derived by the modified retentivity technique. The results shown in figure 3, representing water isothermals on coconut charcoals at 15°C. (F1, steam activated; apparent density 0.534: D1, steam activated (4)) give definite evidence of this rectangular structure when dealing with the desorption points alone (crosses). In figure 4 are shown isothermals of carbon tetrachloride and water on silica gel. In every case there is close agreement between the desorption points and the isothermals derived by the improved technique. Figures are quoted in table 3 which show the variation in quantity values obtained by the two methods.

TABLE 3

ADSORBENT	ADSORBATE	TEMPERATURE	PRESSURE	QUANTITY	
				Desorption points	Improved retentivity method
			mm	*mg/gram*	*mg/gram*
Charcoal D1	H_2O	25°C	11 3	295 1	295 1
			11 0	295 1	295 1
			10 6	277 6	275 7
			10 3	276 8	275 7
			9 8	276 8	275 7
			9 1	270 0	260 3
			8 4	262 4	260 3
			8 1	262 4	260 3
			7 0	232 9	230 8
Silica gel	CCl_4	25°C	8 4	175 8	182 0
			0 9	92 9	89 0
			0 15	48 3	48 3
			0 10	43 0	43 0
Silica gel	H_2O	20 5°C.	6 70	175 0	175 0
			6 10	159 5	159 8
			5 60	147 2	146 7
			4 60	130 3	130.4

DISCUSSION

It has been found (1) that the agreement is good between isothermals obtained by the static technique (air absent) and by the retentivity method, the chief difference being the speed of attainment of equilibrium. In the case of desorption isothermals, using the static technique, the vapor has to diffuse away and this is hindered markedly by the presence of foreign molecules (such as carbon dioxide) on the surface, whereas, in the presence of air, the vapor molecules are removed continuously by the moving stream, together with foreign molecules, the latter method, therefore, causing a quicker cleaning-up and thus a more rapid attainment of equilibrium.

In the case of water desorption isothermals, when desorbing to constant pressure, it is necessary to lower the vapor pressure below that at which a step occurs before the water comprising that step can be removed, hence the pressure at which a step occurs is lower than it would be if all disturbing factors were absent. In the present technique this cannot occur, as one is actually dealing with the quantity adsorbed in an infinitely small layer at the end of the charcoal column, and the pressure over this falls with sudden jumps from one step to another, hence there is no tendency for false equilibria to occur, the pressure drop being sufficiently large to allow all the water sorbed on that step to escape. This aspect will be treated more fully in a future publication on water hysteresis.

The results which have been obtained fully justify this improved technique which is considered to be distinctly in advance of other methods in accuracy and has the additional advantage of being rapid, while giving the exact form of the isothermal over its whole range.

SUMMARY

An improved technique for the determination of isothermals has been described.

The derived isothermals have been found to consist of a series of rectangular steps.

Comparison has been made with points obtained by desorbing to constant pressure.

The author desires to thank Prof. A. J. Allmand for the interest he has taken in this work.

REFERENCES

(1) Burrage: J. Phys. Chem. **34**, 2202 (1930).
(2) Allmand and Burrage: J. Soc. Chem. Ind. **47**, 372T (1928).
(3) Allmand, Burrage, and Chaplin: Trans. Faraday Soc. **28**, 218 (1932).
(4) Allmand and Burrage: Proc. Roy. Soc. London **130**, 610 (1931).

DISCONTINUITIES IN THE SORPTION PROCESS

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INTRODUCTION

In view of the discontinuous nature of desorption isothermals, it appeared to be of interest to establish the presence of these discontinuities in the sorption process. The new technique for the determination of isothermals (see preceding paper), of which brief mention has already been made (1), has shown that when disturbing factors are absent these isothermals consist of a series of rectangular steps. The presence of disturbing effects of various kinds all cause these steps to become curved, in some cases the actual number being increased by the addition of small breaks. The reasons for this will not be discussed here as this subject is dealt with in a further paper in course of preparation.

EXPERIMENTAL

A series of experiments was carried out to determine whether this step-like structure or any indication thereof could be obtained in the sorption process, despite the probability of drift causing disturbances owing to the cleaning-up effect.

Since in other experiments it has been found that the presence of carbon dioxide is a troublesome factor, which often partially vitiates the results, it was decided to carry out three experiments, using (1) a charcoal which had a high capacity for carbon dioxide, (2) one which was fair and (3) one which was poor in this respect, viz.:

(1) Charcoal A (see reference 2)
(2) Charcoal L 1 (Steam activated soft wood. Apparent density 0.445)
(3) Charcoal N 1 (Zinc chloride activated almond shell. Apparent density 0.416)

The procedure adopted was the reverse of the usual retentivity process (3). A column of dry charcoal 60 mm. in length was employed and air saturated with moisture at 11.5 mm. pressure was passed at 400 cc. per minute and 15°C. The air stream was interrupted at very small intervals of time and the adsorption curve constructed, portions of which are shown in figures 1a and 1b.

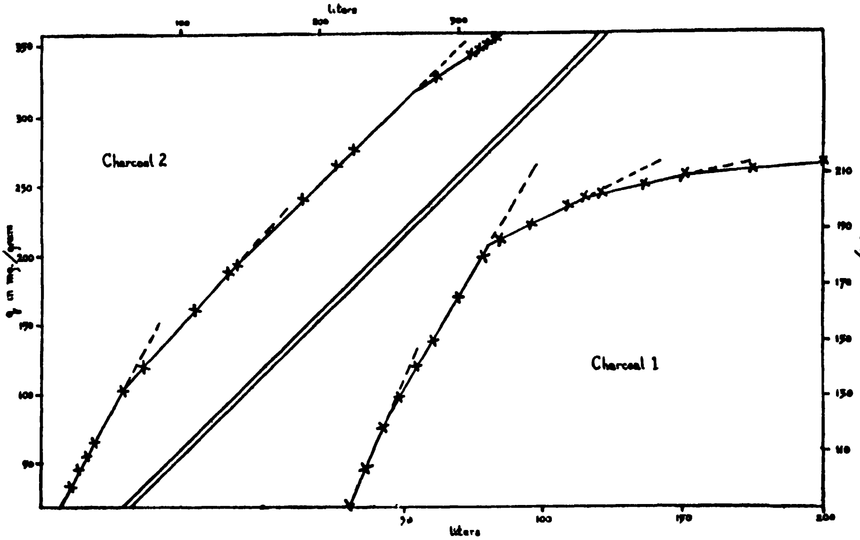

FIG. 1a

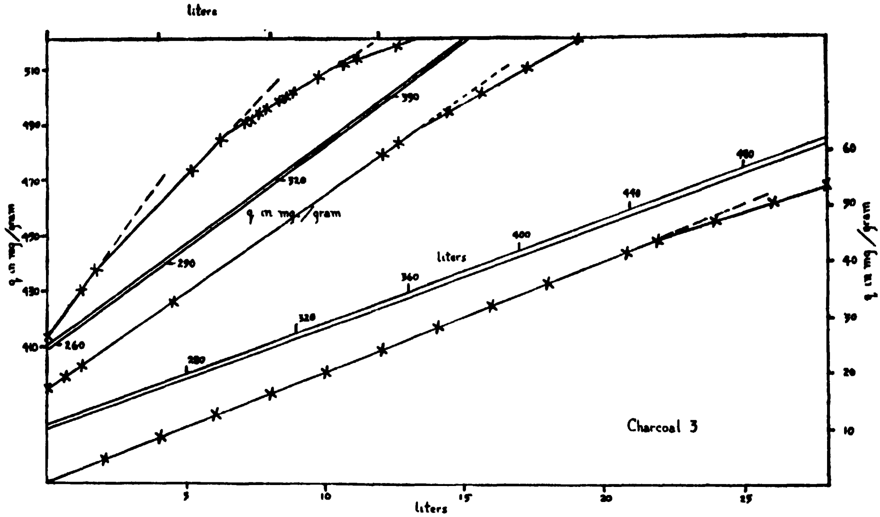

FIG. 1b

DISCUSSION

Figures 1a and 1b show quite conclusively that in spite of small fluctuations, the adsorption-time curves consist of a series of straight lines. These give rise to sorption isothermals shown in figure 2.

The pressure is calculated in the following manner: From the slopes of the linear portions of the retentivity curve, the weight of vapor adsorbed in a given time is obtained. Knowing the pressure, and therefore the quantity of vapor in the charging stream in the same period of time, the difference between this and the amount adsorbed represents the weight of vapor in the effluent gas, this giving the pressure of vapor over the end of the charcoal column.

These pressures are correct but the isothermals are approximate, since in each case the quantity is not a "true" value but an average one, for it represents the total water in the column expressed as milligrams per gram of charcoal and not that amount corresponding to the last layer of the charcoal column. This in no way vitiates the results, as the object of the present investigation was to demonstrate that sorption takes place in rectangular steps. This is shown by the pressure remaining constant over a given quantity range, irrespective of whether the quantity concerned is an average or true value. Figure 2 shows clearly that the sorption isothermal occurs in rectangular steps, the individual points being omitted except for those marking the beginning and end of these steps.

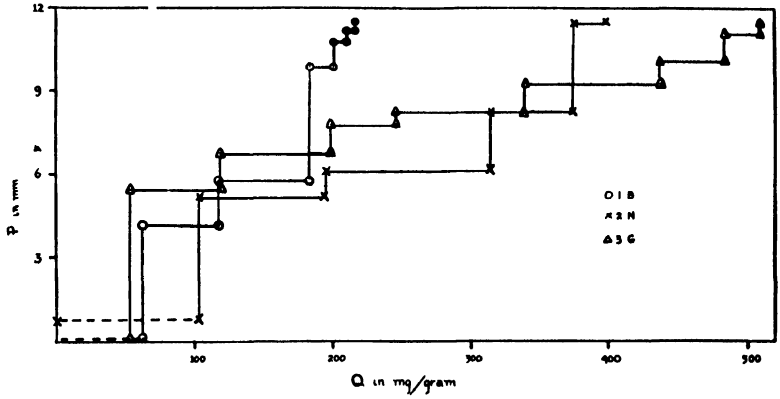

Fig. 2

Instead of ignoring the slight deviations from the straight lines in figures 1a and 1b, the average rate of adsorption between each two successive points was calculated and assumed to hold at the middle point of the time interval (figures 3a and 3b). If there were no disturbing factors the rate of adsorption along a step would be constant, the rate-time diagrams appearing in rectangular steps. Figures 3a and 3b, which greatly magnify the errors, show that (1) is the least rectangular, (2) more so, and (3) fairly well defined. These results fall in the inverse order of their capacity for carbon dioxide, as one might have expected. The carbon dioxide evolved during each run was noted qualitatively by passing the effluent gas through baryta water and noticing the change in depth of turbidity. In this connection it is of interest to note that the sudden increase in the rate of adsorption (figure 3b, point *) was definitely associated with a greatly increased evolution of carbon dioxide.

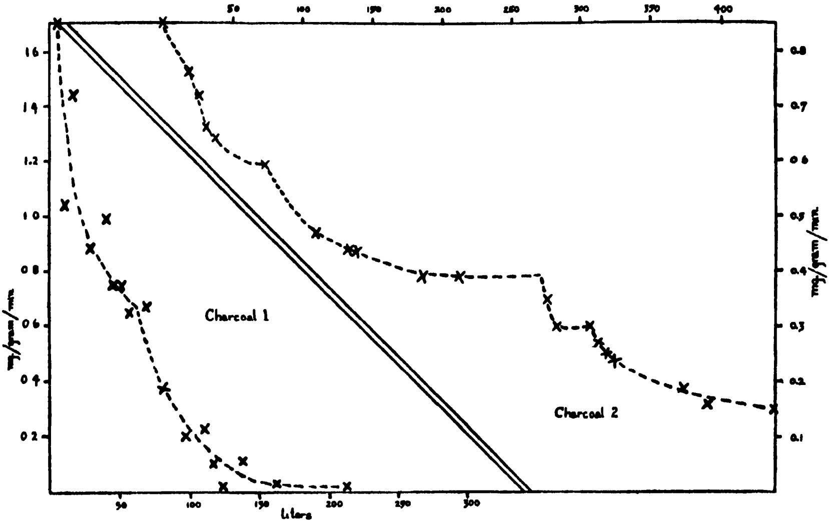

Fig. 3a

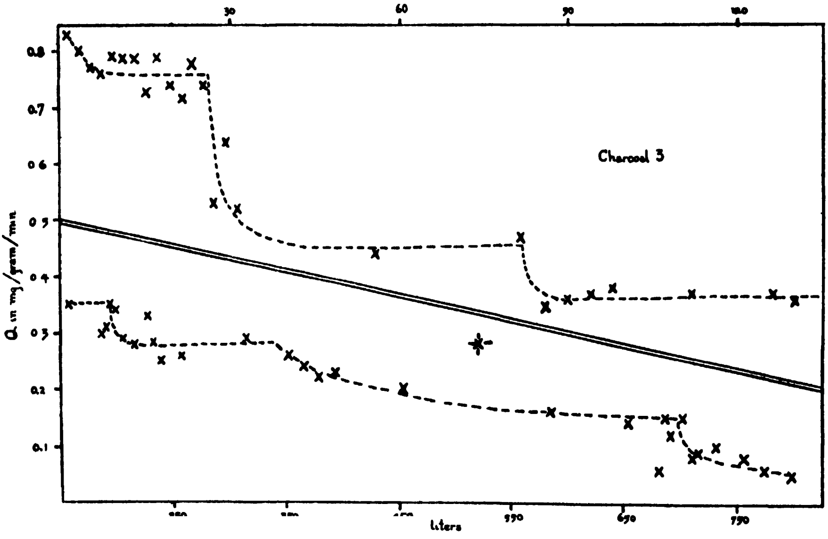

Fig. 3b

In figure 2, the pressure figures for the lowest step in each case can be neglected, as several smaller steps whose pressures are close together are represented here and one cannot accurately determine them. In general there is a tendency for the quantity per step to be small at low pressures, larger at intermediate and smaller again at higher pressures, similarly to that found in desorption isothermals.

To facilitate comparison with the pressures at which the steps occur in desorption isothermals to be submitted in a later publication the pressures at which the steps occur have been tabulated.

Charcoal 1	*Charcoal 2*	*Charcoal 3*
4.1 mm.	5.1 mm.	5.5 mm.
5.8 mm.	6.2 mm.	6.7 mm.
9.9 mm.	8.2 mm.	7.8 mm.
10.8 mm.	11.5 mm.	8.2 mm.
11.2 mm.		9.2 mm.
		10.1 mm.
		11.1 mm.

SUMMARY

Sorption isothermals have been shown to consist of a series of rectangular steps similar to desorption isothermals.

The effect of the carbon complex (C_xO_y) on the rate of adsorption has been noted.

The pressures at which steps have been found to occur have been tabulated for different charcoals.

REFERENCES

(1) Allmand, Burrage, and Chaplin: Trans. Faraday Soc. **28,** 218 (1932).
(2) Hand and Shiels: J. Phys. Chem. **32,** 441 (1928).
(3) Allmand and Burrage: J. Soc. Chem. Ind. **47,** 372 (1928).
Burrage: J. Phys. Chem. **34,** 2202 (1930).

A NOTE ON THE SORPTION OF WATER VAPOR BY GLASS

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Received October 3, 1932

A study of the condition of water in coals of various ranks which is now in progress in this laboratory requires a knowledge of the sorption of water vapor by the glass system used in the investigation, over a range of pressures from 10 to 1000 microns at temperatures varying from 25° to 30°C. The data available over this range are very meagre. Frank (1) has made a very precise measurement from 1 to 100 microns at 20°C. but the writers know of no published data, other than Frank's, which are reliable below 50 per cent relative humidity. Although the data were required simply to furnish a correction factor, it seemed unwise to extrapolate Frank's isotherm to 1000 microns, not only because of the effect of varying previous histories of Frank's glass and that of the authors, but also because the water vapor–glass isotherm must show a point of inflection somewhere between a relative humidity of 0.006, which is the upper limit of Frank's isotherm, and a relative humidity of 0.5, which is the lower limit attained by McHaffie and Lenher (2). Such a point of inflection must exist, since Frank's isotherm is *concave* toward the pressure axis while that of McHaffie and Lenher is convex. It was primarily to receive assurance that this point of inflection did not occur below 3.5 per cent relative humidity that the measurements herein described were made.

APPARATUS AND PROCEDURE

The apparatus is shown in figure 1. S_1, S_2, S_3, S_4 and S_5 are mercury seal stopcocks. T_1 contains the coal and was shut off at S_3 during these measurements. T_4 is used in the study of coal and is of no significance in these measurements. F is a 12-liter Pyrex flask and M a mercury manometer. This manometer was made from 17-mm. Pyrex tubing and, after careful cleaning, was sealed empty to the apparatus. It was then "torched out" under high vacuum for half an hour, and after cooling mercury was distilled into it through a side arm (not shown). It was read with a micrometer microscope and calibrated against the McLeod gauge, using dry air as the calibrating gas. It was self-consistent to one micron at pressures below 100 microns and its absolute accuracy was about one per cent at the highest pressure measured (ca. 1700 microns).

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[2] Director, Mineral Industries Research.

T_2 is a tube of distilled water kept at a constant temperature by the thermostat B. The volume between S_4 and S_5 including T_3 was measured before sealing to the apparatus. By closing S_4 and opening S_5, T_3 was saturated with water vapor at a pressure calculable from the temperature of the thermostat. Then by closing S_5 and opening S_4 a definite weight of water was introduced into the system.

Since the thermostat was operating only slightly below room temperature, the relative humidity in T_3 was fairly high, and it was necessary to add to the weight of water vapor in its free space the weight sorbed on the walls in order to calculate the weight of water vapor added to the system. This correction, which did not exceed 10 per cent of the total weight introduced, was obtained from McHaffie and Lenher's isotherm for high relative humidities.

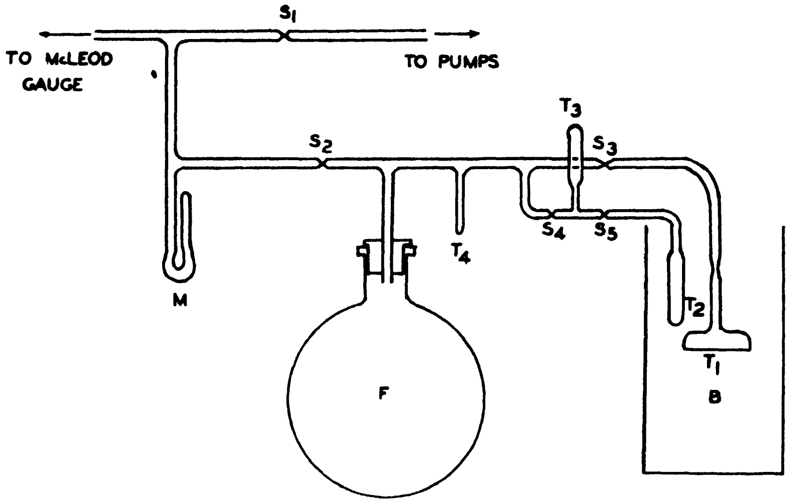

FIG. 1. APPARATUS FOR STUDYING AQUEOUS TENSION OF WATER IN COAL

As it was not convenient to thermostat the entire apparatus, consistent results were not easy to obtain, but by exercising some care to keep the laboratory temperature fairly constant, it was possible to test the rectilinear character of the relationship between the logarithms of relative humidity and the weight sorbed per unit area over the range in question.

Before starting a measurement, the system was pumped to a high vacuum (10^{-6} mm. or better) and pumping was continued for at least twelve hours. The glass was therefore "dry" in the ordinary sense, but it must be remembered that several days exposure to a vacuum of 10^{-6} mm. are necessary to remove the last traces of moisture at ordinary temperatures.

RESULTS

The data obtained are given in tables 1 and 2 and are shown graphically in figure 2. In the tables W, W_f, and W_g are, respectively, the weight of water vapor introduced, the weight in the free space (as calculated from the observed pressure), and the weight sorbed, all in grams × 10^3. W_g/A is the weight sorbed per unit area. P is the pressure in microns and $R. H.$ is the relative humidity × 10^3.

TABLE 1

Isotherm at 302°K.

W	P	W_f	W_g	W_g/A	R H
0 58	41	0 476	0 104	2 9	1 4
1 16	86	1 00	0 16	4 5	2 9
1 74	133	1 54	0 20	5 5	4 5
2 32	182	2 11	0 21	5 9	6 1
2 90	731	2 68	0 22	6 2	7 8
3 48	277	3 21	0 27	7 5	9.3
4 06	375	3 77	0 29	8 2	11 0
4 64	374	4 34	0 30	8 5	12 6
5 22	423	4 91	0 32	8 9	14 2
8 70	717	8 32	0 38	10 7	24 1
11 60	960	11.15	0 45	12 7	32.3

TABLE 2

Isotherm at 298 5°K

W	P	W_f	W_g	W_g/A	R H
0 542	37	0 436	0 109	3 1	1 5
1 08	78	0 92	0 16	4 5	3 2
1 65	123	1 45	0 20	5 6	5 1
2 17	164	1 94	0 23	6.5	6 8
2 71	207	2 44	0 27	7 6	8 6
3 26	250	2 95	0 31	8 7	10 4

Figure 2 is a logarithmic plot of the results and clearly shows the rectilinear character of the isotherm over the range in question. In figure 2 appears a line lying to the left of the experimental curve and with a slightly steeper slope. This is Frank's isotherm, shown as a solid line over the range of his observations and extrapolated as a broken line to cover the range of the authors' measurements.

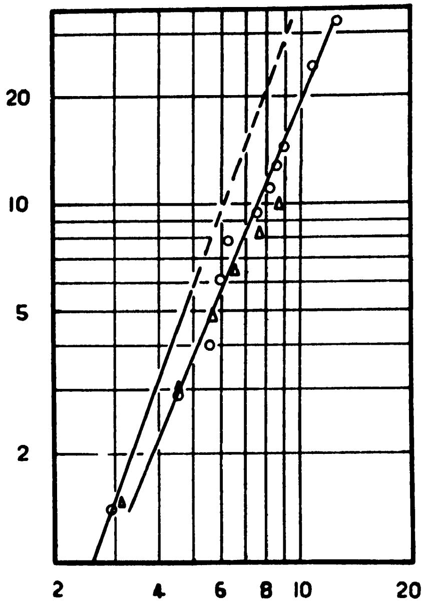

FIG. 2. SORPTION OF WATER VAPOR BY GLASS

The logarithms of the relative humidities × 10^3 are plotted as ordinates against the logarithms of weight sorbed in grams × 10^8 per sq. cm. as abscissae. Centers of circles are points obtained at 302°K. Vertices of triangles are points obtained at 298.5°K.

DISCUSSION

The results obtained are somewhat higher than Frank's. There are three factors which may account for the difference. First, a difference in the composition and history of the glass; second, a difference in the extent of drying before beginning a measurement; third, an error in McHaffie and Lenher's results used to correct the computation of the weight of water introduced.

It seems unlikely that the use of McHaffie and Lenher's data could introduce serious error, through being itself at fault, not only because it was used for making a fairly small correction, but also because of the good agreement between the two corrections made from quite different points on their isotherm. At 258.5°K. the correction is about 4 parts in 53 and at 302°K. it is about 2 parts in 56, and yet the writers' measurements at these two temperatures as corrected by McHaffiie and Lenher's data are in good agreement.

It is impossible to consider the second source of discrepancy, because Frank says simply that his adsorption chamber was "dried under vacuum." If Frank pumped his glass for considerably shorter periods of time than was used in these measurements, his results would, of course, be lower than those obtained in this laboratory.

It seems most probable that the chief source of difference lies in a different treatment of the glass. Frank allowed his glass to stand in contact with chromic acid for one week, during which time the acid was boiled several times. He thereafter cleaned the glass by soaking in distilled water and rinsing with conductivity water. The writers' sorption chamber was cleaned with boiling soap solution and rinsed with hot distilled water, and was then subjected to steam at atmospheric pressure for four hours. It was thereafter rinsed with hot distilled water several times before being attached to the system.

SUMMARY

A test of the rectilinear character of the logarithmic form of the sorption isotherm for the system water vapor–glass has been made over a range of relative humidities from 10^{-3} to 3×10^{-2}.

The results agree closely with the very precise measurements of Frank and indicate that his isotherm may be extrapolated to include pressures of the next higher order of magnitude.

The authors wish to express their thanks to the National Research Council for a Grant-in-Aid which made the study on the condition of water in coal possible.

REFERENCES

(1) Frank, H. S.: J. Phys. Chem. **33**, 970 (1929).
(2) McHaffie, I. R., and Lenher, S.: J. Chem. Soc. **127**, 1561 (1925).

THE EFFICIENCY OF CARBON DIOXIDE AS A RADIOCHEMICAL CATALYST

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Received July 29, 1932

The catalytic effect of carbon dioxide on the combination of carbon monoxide and oxygen in the presence of radon was found to be very small (1), only 14.5 per cent of the total ionization falling upon the sensitizing gas being utilized in promoting the reaction. That this low efficiency of carbon dioxide is characteristic of the gas is seen also from its effect on the radiochemical acetylene polymerization.

For the normal reaction in a sphere of 1.933 cm. diameter (2), the $-\frac{M_{C_2H_2}}{N_{C_2H_2}}$ ratio is 19.8, where $M_{C_2H_2}$ is the number of acetylene molecules disappearing from the gas phase, and $N_{C_2H_2}$ is the number of ion pairs produced in the gas by the alpha-particles from radon in equilibrium through RaC. The same M/N ratio was found for the greater part of the polymerization when sensitized by inert gases such as helium and neon (3), after correction was made for the ionization falling on the catalyst by assuming 100 per cent efficiency of the inert gas. That this assumption fails for the influence of carbon dioxide on this reaction is shown by the abnormally low initial $-M/N$ value of 16.4, which steadily decreases as the reaction proceeds. Table 1 taken from unpublished work of Lind and Bardwell[2] presents these data in detail.

Column I shows the decreasing $-M/N$ values calculated on the assumption of 100 per cent transfer of ionization on carbon dioxide to the reacting acetylene molecules.[3] However, more than 14.5 per cent of the carbon dioxide ionization is effective in speeding up the reaction, as is seen by inspecting columns II and III. Calculations in column II are based on the assumption of a 14.5 per cent catalytic efficiency[4] as was found in the carbon monoxide oxidation. Correcting for a fractional efficiency of 30 per cent, column III contains a satisfactory constant M/N

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[1] Du Pont Fellow in Chemistry at the University of Minnesota, 1930–1931.

[2] These data are included with the kind permission of Professor S. C. Lind of the University of Minnesota.

[3] For details of this calculation see reference 3.

[4] For details of this calculation see reference 1.

ratio averaging 22.2, which is quite comparable with the value of 20 to be expected in a sphere of the size used. This small discrepancy of 10 per cent is readily accounted for when it is recalled that the measured reaction velocity, and therefore the M/N value, is approximately 10 per cent too high because of the disappearance of a small quantity of carbon dioxide from the gas phase.

That the efficiency of carbon dioxide in this reaction is greater than in

TABLE 1

The effect of carbon dioxide on the acetylene polymerization

$$x\ C_2H_2(g) + CO_2(g) = (C_2H_2)_x + CO_2(g)$$

D = 1 930 cm ; E_0 = 0 0141 curie radon

$e^{-\lambda t}$	$P_{C_2H_2}$	P_{CO_2}*	P_{H_2}	−M/N RATIO		
				I (assuming 100 per cent efficiency)	II (assuming 14 5 per cent efficiency)	III (assuming 30 per cent efficiency)
	mm Hg	*mm* Hg	*mm* Hg			
1 0000	557 5	561 5	0 0			
0 9668	460 3	550 5	1 2	16 39	27 7	24 3
0 9578	436 1	547 8	1 5	10 38	29 3	25 2
0 9489	413 5	545 2	1 8	15 15	26 4	22 9
0 9208	349 9	538 0	2 7	13 82	26 6	22 4
0 8981	304 9	533 0	3 5	13 02	26 2	21 8
0 8384	200 3	521 3	5 2	12 82	28 7	23 0
0 8167	171 1	517 9	5 7	10 78	27 3	20 9
0 7866	133 0	513 6	6 3	10 78	29 6	22 1
0 7534	95 9	509 5	7 3	10 08	31 5	22 2
0 6720	25 4	501 5	8 4	8 6	34 9	21 5
0 5828	0 0	498 5	9 4	3 1	16 6	9 0
						Av. = 22 2

* About 35 mm. of the total of 63 mm of carbon dioxide was recovered by heating the solid reaction product, indicating that the loss of carbon dioxide resulted from mechanical trapping of the gas.

the carbon monoxide oxidation may be due to the relative ionization potentials of 14.4 (4) and 11.6v (5) for carbon dioxide and acetylene respectively, a condition favorable to a flow of ionization from the catalyst to reactant (6). It appears that only a small part of the carbon dioxide ionization is available even in this reaction where conditions are favorable for a pronounced catalytic effect.

Of greater interest is the behavior of carbon dioxide in the presence of a hydrogen–oxygen mixture. This two component system is similar to the $2CO:1O_2$ system. The stoichiometric relations are identical, both reaction products are radiochemically inert (7), and the relation between ionization potentials of components is the same for both systems. Accordingly, the catalytic efficiency of carbon dioxide in the water synthesis under the influence of radon should be very small and approximately that found in the carbon monoxide oxidation.

A possible objection to the execution of this experiment was the chance for reduction of carbon dioxide by hydrogen (8) which would mask any catalytic effect. However, oxidation was found to be as exclusive here as it was in other reactions (2). Measurements at liquid air temperatures showed no appreciable loss of carbon dioxide until the greater part of the reactants had been used up.

TABLE 2

The effect of carbon dioxide on the water synthesis

$2H_2(g) + 1O_2(g) + CO_2(g) = 2H_2O(l) + CO_2(g)$

$D = 2.006$ cm.; $E_0 = 0$ 105 curie radon; $P_{CO_2} = 215$ 9 mm.

$e^{-\lambda t}$	$P_{(2H_2 + 1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_c$	$\left(\frac{k\mu}{\lambda}\right)'_{corr}$
	mm Hg		
1 0000	456 7		
0 9400	376 9	30 5	25 1
0 9139	347 5	29 7	23 6
0 8869	319 3	29 9	23 4
0 8511	286 1	29 3	22 4
0 8228	261 5	30 3	22 6
0 8198	(259 8)*		
0 7808	231 2	28 0	20 3
0 7284	195 1	30 9	21 5
0 6873	171 0	30 6	20 3
0 6847	(177 3)*		
0 6473	149 7	31 7	20 1
0 5949	125 2	32 6	19 4
0 4689	81 5	32 5	16 9
0 4006	64 5	32 7	14 3
0 3333	50 6	34 4	13 1
0 2315	35 7	32 7	10 3

* Pressures in parentheses were measured at liquid air temperatures.

The reaction mixture was prepared by adding carbon dioxide to a 2:1 mixture of hydrogen and oxygen obtained by electrolysis of a 10 per cent potassium hydroxide solution. This mixture was confined in a small spherical vessel containing a known quantity of radon, and the reaction was followed manometrically. Table 2 shows the course of the water synthesis in the presence of carbon dioxide. The column headed $\left(\frac{k\mu}{\lambda}\right)'_c$ was calculated from the usual expression for velocity constants in radiochemical reactions (9),

$$\left(\frac{k\mu}{\lambda}\right)' \quad \frac{2.303\ \Delta\log P_{(2H_2+1O_2)}}{E_0\ \Delta e^{-\lambda t}}$$

ignoring the correction for ionization on carbon dioxide. In this equation $e^{-\lambda t}$ is the fraction of radon left after time t, E_0 is the initial quantity of radon in curies, λ is the decay constant of radon and $P_{(2H_2+1O_2)}$ is the partial pressure of the stoichiometric mixture at time t. The column headed $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is the velocity constant of the catalyzed reaction correcting for the fractional efficiency of carbon dioxide according to the expression,

$$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \quad \frac{2.303\ \Delta\log\left[P_{(2H_2+1O_2)} + x\,\frac{i_{CO_2}}{i_{(2H_2+1O_2)}}\,P_{CO_2}\right]}{E_0\ \Delta e^{-\lambda t}}$$

where $x = 0.145$, the specific ionizations i_{CO_2} and $i_{(2H_2+1O_2)}$ are 1.52 and 0.53, and the initial $P_{CO_2} = 215.9$ mm. The ionic equivalent of the carbon dioxide

$$\left[x\,\frac{i_{CO_2}}{i_{(2H_2+1O_2)}}\,P_{CO_2}\right]$$

is therefore 90.3 mm.

From the inverse square law (9), we should expect the velocity constant to equal 21.5 in a sphere of 2.006 cm. diameter. Evidently $\left(\frac{k\mu}{\lambda}\right)'_c$ is too high, indicating a decided catalytic effect of the carbon dioxide. Assuming the same efficiency of 14.5 per cent as found in the carbon monoxide oxidation, column $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is obtained. Though not strictly constant, as shown by the decreasing $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr}}$ values, this correction is plainly of the proper order of magnitude. The decreasing velocity constants are in accord with the "depletion effect" which is characteristic of radiochemical reactions (3) sensitized by inert gases. This effect sets in when more than half of the total ionization falls on the catalyst. In the reaction considered in table 2, considerably more than half of the total initial ionization is falling on the carbon dioxide because of the great difference in specific ionization values of the reaction mixture and the catalyst. It is, therefore, not surprising that a decrease in the corrected velocity constant is obtained as the reaction proceeds.

This result is comparable with the effect of argon on the water synthesis. Here, too, a pronounced depletion effect is reported (3).

DISCUSSION

When Lind and Bardwell first discovered the pronounced catalytic effect of inert gases on radiochemical reactions, they assumed that the ionization falling on the foreign gas was completely effective in producing the reaction involved. Many of the cases studied justified this assumption. Thus, until the depletion effect sets in, helium, krypton, neon, and nitrogen are very efficient radiochemical catalysts.

Applying this assumption to catalysis by argon, xenon and carbon dioxide, the calculated values of velocity constants and M/N ratios are below those normally found for the reaction studied. The effect of carbon dioxide formed in the carbon monoxide oxidation was so small as to necessitate a study of its direct effect by the addition of a large initial quantity of the dioxide to a stoichiometric carbon monoxide–oxygen mixture. The results of this work showed carbon dioxide to have a definite effect on the reaction, but one which was small when compared with the efficient atmospheric gases mentioned. That this behavior of the dioxide is a characteristic property can readily be seen from its effect on the water synthesis and the acetylene polymerization. Thus in all three reactions where the effect of carbon dioxide has been investigated, it has been shown to be a very inefficient catalyst.

One must then attribute to every gaseous sensitizer a characteristic ability to accelerate radiochemical reactions, whether the effect results from direct clustering about the inert gas ions or from transfer of ions to reactants followed by clustering about reactants. Why certain gases, say helium and neon, should have a greater catalytic effect than others, such as carbon dioxide and argon, is not immediately evident; but the empirically determined fact remains that the efficiency of these gases varies.

From the point of view of a clustering mechanism, inefficiency of catalysts in these reactions may be interpreted as a tendency for neutral inert gas molecules to cluster about gaseous ions which would otherwise form clustering centers for reacting molecules. This crowding out effect has been suggested by Lind and Rosenblum to explain the course of the carbon monoxide oxidation.

It is, furthermore, reasonable to regard the depletion effect as resulting from a diminished efficiency of the inert gas, as an increasingly greater portion of the total ionization falls upon it. A simultaneous decrease in the concentration of reacting molecules creates a situation favorable towards a crowding out of reactants from clusters by inert gas molecules, accounting for the diminishing catalytic effect of even efficient inert gases as reactions approach completion.

SUMMARY

Carbon dioxide was shown to be an inefficient catalyst in radiochemical reactions. In the water synthesis, its efficiency is similar to that in the carbon monoxide oxidation, namely 14.5 per cent. Even in the acetylene polymerization, a case conducive to a pronounced catalytic effect, only about 30 per cent of the carbon dioxide ionization is utilized in promoting reaction.

It is suggested that the inefficiency of a radiochemical catalyst is governed by the tendency of the inert gas to cluster about gaseous ions crowding out reactant molecules, and that the greater this tendency, the less efficient the catalyst. The depletion effect is considered as resulting from a lowered efficiency of the catalyst, as the quantity of reactant decreases and as a greater portion of the total ionization falls upon the catalyst.

REFERENCES

(1) LIND AND ROSENBLUM: Proc. Nat. Acad. Sci. **18**, 374 (1932).
(2) LIND, BARDWELL, AND PERRY: J. Am. Chem. Soc. **48**, 1556 (1926).
(3) LIND AND BARDWELL: J. Am. Chem. Soc. **48**, 1575 (1926).
(4) SMYTH AND STUECKELBERG: Phys. Rev. **36**, 472 (1930).
(5) TATE AND SMITH: Phys. Rev. **39**, 270 (1932).
(6) SMYTH, HARNWELL, HOGNESS, AND LUNN: Nature **119**, 85 (1927).
(7) DUANE AND SCHEUER: Le Radium **10**, 33 (1913).
LIND AND BARDWELL: J. Am. Chem. Soc. **47**, 2675 (1925).
(8) LIND AND BARDWELL: J. Am. Chem. Soc. **47**, 2675 (1925).
(9) LIND: J. Am. Chem. Soc. **41**, 531 (1919).

THE CHEMISTRY OF BERYLLIUM. V

ORGANIC COMPOUNDS OF BERYLLIUM[1]

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Received August 3, 1932

INTRODUCTION

The organic compounds of beryllium have been very little studied. There have been many attempts to produce beryllium salts of organic acids, such as succinic, malonic, salicylic, and the fatty acids (1), but with the exception of beryllium trichloroacetate the products (2) have been mixtures of beryllium hydroxide with the respective acids, owing to the fact that they were prepared by neutralizing the acid with beryllium hydroxide or carbonate. Since solutions of beryllium salts (3) dissolve large amounts of beryllium hydroxide the products were contaminated by this excess. Some (4) have tried to overcome this difficulty by using an excess of the organic acid, but it is evident that this procedure must yield impure products except when the solubilities of the acid and salt differ enough to permit separation by recrystallization. Even this is often impossible because many beryllium salts hydrolyze as soon as the acid is removed. The trichloroacetate furnishes an example of this. This difficulty might be obviated by crystallization from organic solvents.

These mixtures were long thought to be true compounds because: (1) when washed with alcohol the products were finely granular although they showed no true crystals under the microscope; (2) the determination of their composition was based solely on the beryllium oxide content which we now know varies with temperature, concentration of acid, and amount of beryllium hydroxide or carbonate used; (3) the methods generally used for determining their molecular weights were inaccurate, because beryllium hydroxide dissolves in solutions of its normal salts, causing the freezing points to be abnormal (5).

A simple and satisfactory solution of the problem of their preparation in a pure state, at least in the case of the sulfonates, is described in this paper by a method which does not seem to have been used before. The beryllium salts were prepared by double decomposition of barium salts of the respective acids with beryllium sulfate. This method is not applicable to the preparation of easily hydrolyzed compounds, but the fact that the sulfonates are gummy when prepared by neutralization would seem to indicate that previous failure might not be due entirely to hydrolysis but partly to the excess of hydroxide dissolved by the beryllium salt solution. The extreme solubility of beryllium sulfonates made recrystallization from water impracticable and therefore mixtures of organic solvents were used.

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[1] For former articles on beryllium, see This Journal 35, 2465, 2492, 3111 (1931); 36, 2641 (1932).

To establish the definite chemical nature of the compounds (1) they were examined with the polarizing microscope; (2) the compounds were not analyzed in the usual way by ignition to oxide but after thorough drying were completely decomposed by fuming nitric acid in Carius tubes, and analyzed not only for the beryllium content, determined by the ignition of the precipitated hydroxide, but also for sulfate; (3) as a further proof a molecular weight determination was made by the boiling point rise method with acetone as solvent.

PREPARATION AND PURIFICATION OF MATERIALS

The ethyl acetoacetate, the ethyl benzoate, the benzene, chloroform, dichloromethane, carbon disulfide, sulfonic acid, and carbon tetrachloride used were pure chemicals as obtained. Acetophenone was redistilled. The acetone was dried over anhydrous sodium sulfate and redistilled. Toluene was stood over barium oxide for five hours, then distilled, and the fraction boiling at 108.5°C. was used.

Barium hydroxide

The crude barium oxide[2] was placed in a large evaporating dish and distilled water was added slowly, but rapidly enough to keep up a vigorous evolution of steam. When the addition of water caused no further reaction, the boiling hot mixture was poured quickly into another large evaporating dish full of distilled water to yield white crystals of barium hydroxide octahydrate. This mixture was brought to a boil, a few grams of barium peroxide were added to oxidize iron compounds, the mixture was boiled for 5 minutes and then allowed to cool, yielding colorless crystals of barium hydroxide octahydrate, iron free.

Beryllium sulfate tetrahydrate was made by evaporating pure beryllium nitrate tetrahydrate crystals, made from purified beryllium hydroxide, with concentrated sulfuric acid until no fumes were noticeable (6). The product was twice recrystallized.

Melting points were determined by the usual capillary method using a 360° thermometer calibrated at the highest point, at the transition point of sodium sulfate decahydrate, at the steam point, and at the melting point of pure tin. For the determination of decomposition points the samples were heated in capillary tubes in a fused mixture of sodium and potassium nitrates. The molecular weights were determined by the boiling point method, using the electrically heated Beckman apparatus.

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[2] Kindly furnished by Mr. M, J. Rentschler, J. H. R. Products Company, Willoughby, Ohio.

ANALYSES

All the compounds except beryllium dibenzoylmethane were decomposed by fuming nitric acid in Carius tubes and the beryllium was determined by precipitation with ammonium hydroxide as beryllium hydroxide and ignition to beryllium oxide. In the case of the sulfonates the filtrates from the beryllium hydroxide precipitate were used for the determination of the sulfates by precipitation as barium sulfate.

PART I

SULFONATES OF BERYLLIUM

As stated before, the sulfonates of beryllium cannot be made pure by neutralizing solutions of the sulfonic acids with beryllium hydroxide or beryllium carbonate, because solutions of beryllium salts dissolve beryllium hydroxide, the solutions remaining acid to litmus although they contain a large excess of beryllium hydroxide. Crystals sometimes separate from these solutions after several months, but they are gummy and coated with beryllium hydroxide. Too little attention to this has been the cause of serious error in the past (7). An exception to this is the recent work of Sidgwick and Lewis (4) who prepared beryllium benzenesulfonate and beryllium *p*-toluenesulfonate by evaporating a mixture of the hydroxide with a slight excess of the acid. The salt crystallized out on cooling a concentrated solution. They stated that both sulfonates separated with four molecules of water, but they did not obtain the anhydrous salts, because they decompose on heating. They based the composition simply on the weight of beryllium oxide obtained by ignition. They did not make a detailed study because the salts were not suitable for their purpose.

If the salts are made by neutralization, they may be separated from concentrated solutions containing beryllium hydroxide by precipitating the hydroxide with absolute alcohol, in which the beryllium salts are soluble, followed by filtering, and allowing the filtrate to evaporate. Even then, the crystals are gummy. If these crystals are allowed to stand for several months, the beryllium hydroxide becomes inactive and finally dehydrated, and will no longer dissolve in absolute alcohol, so that if the mixture is now dissolved in alcohol and filtered, good crystals may be obtained from the filtrate. This method is too slow and uncertain to be practicable.

In this laboratory a quick and easy way to prepare the pure salts was found to be by double decomposition of the barium salts with beryllium sulfate. The acid was neutralized with pure barium hydroxide, filtered, and evaporated to incipient crystallization. Most of the barium salts are beautifully crystalline and not very soluble. They were recrystallized from water when necessary. A solution of the pure salt was then mixed with one of beryllium sulfate, until further addition of either caused no precipitation. This point was determined by filtering a small portion of the mixture till clear, dividing into two portions, and testing one with a few drops of the solution of the barium salt and the other with the solution of beryllium sulfate. The mixtures were allowed to stand ten minutes. When exactly the right amount of beryllium sulfate had been added, the solution was digested to enlarge the barium sulfate particles, filtered, and evaporated nearly to dryness. If heated too strongly, or if evaporated to dryness, some of the salts hydrolyze or char, so the evaporation was completed in a vacuum desiccator. In some cases, crystals containing water of crystallization formed after the water had almost entirely evaporated. In other cases, only a crystalline mass remained. The products had to be dried in an over before they could be crystallized from organic solvents, because too much water prevents the formation of good crystals, and even if a precipitate does form, it partially redissolves. However, some water was evidently left in the salts, because the solvents used were free from water, and yet the products contained water of crystallization.[3] The salt was dissolved in as small a quantity of acetone as possible, and the toluene, carbon tetrachloride, or chloroform was added until considerable precipitate had been formed. The mixtures were then filtered as quickly as possible. Fine crystals separated at once. These were redissolved by heating the mixture. It was then allowed to cool slowly. Mixtures of toluene and acetone, carbon tetrachloride and acetone, or chloroform and acetone were found to be the best solvents from which to recrystallize them.

All these salts show polarization colors when examined under the microscope by polarized light. In dry acetone solution, the dried salts are not acid to litmus, but after a few moments exposure to the air, enough moisture is condensed on the surface of the solution to cause hydrolysis, and the litmus turns pink. All the sulfonates dissolve at once in liquid ammonia, and beryllium hydroxide is precipitated if the ammonia is not dry.

The analyses and the fact that the microscope showed only one kind of crystal in each case, indicate that the products are pure. The molecular weight determination shows that, when dry, they are not associated or combined with the solvent.

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[3] The exact amount was not determined in all cases because we were interested in obtaining anhydrous salts, but the melting points showed that several hydrates exist for each salt.

Beryllium p-toluenesulfonate

$[C_6H_4(CH_3)SO_3]_2Be$

Beryllium *p*-toluenesulfonate crystallizes from a mixture of acetone and chloroform in colorless, monoclinic needles containing water of crystallization. This may be driven off by drying in an oven, if the temperature is raised slowly enough. After being dried several hours at 190°C., the salt does not melt until it decomposes at 318.5°C. (cor.). The analysis also shows that all the water has been driven off.

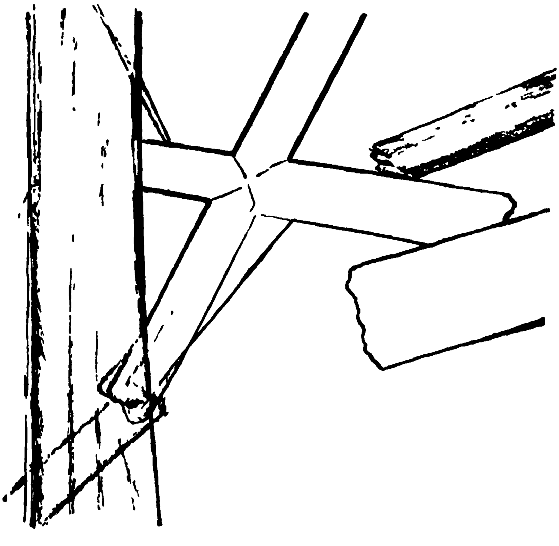


FIG. 1. BERYLLIUM *p*-TOLUENESULFONATE

Beryllium *p*-toluenesulfonate is very soluble in water, absolute alcohol, and acetone, and insoluble in ether, benzene, and dichloromethane. It is insoluble in cold glacial acetic acid, but very soluble in hot. It may be crystallized from water, but its extreme solubility makes this impracticable.

When crystallized from a mixture of acetone and chloroform, it melts in its water of crystallization at 133.8°C. (cor.), and again at 143.5–145.5°C. (cor.). It appears to lose water from 120°C. up, even if the capillary tubes are sealed. It decomposes at 318.5–319.5°C. (cor.).

Analysis. (1) 0.2078 gram sample gave 0.0154 gram BeO and 0.2760 gram $BaSO_4$. Calculated: BeO, 7.14; S, 18.25. Found: BeO, 7.41; S, 18.24. (2) 0.1902 gram sample gave 0.0142 gram BeO and 0.2558 gram $BaSO_4$. Calculated: BeO, 7.14; S, 18.25. Found: BeO, 7.47; S. 18.47.

Beryllium p-xylenesulfonate

$[C_6H_3(CH_3)_2SO_3]_2Be \cdot 5H_2O$

Beryllium *p*-xylenesulfonate, unlike the other sulfonates, crystallizes readily from water solution. It may be boiled to dryness without decomposition, although solutions are acid to litmus. Since it is not hydroscopic, like the other sulfonates, the water of crystallization was easily determined, by drying in an oven at 140°C. It was found to contain five molecules of water of crystallization.

Large, perfect crystals may be readily obtained on slowly cooling a hot water solution, if the concentration is correct. They are apparently monoclinic, having an extinction angle of 9° in one position, and showing parallel extinction in the other two. When thin, the crystals exhibit brilliant polarization colors.

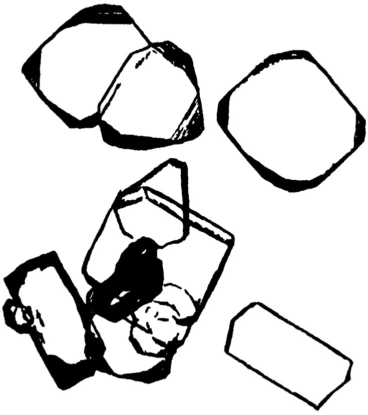


FIG. 2. BERYLLIUM *p*-XYLENESULFONATE

Beryllium *p*-xylenesulfonate is very soluble in water, absolute alcohol, hot glacial acetic acid, and acetone, and insoluble in ether, benzene, carbon tetrachloride, toluene, chloroform, dichloromethane, and carbon disulfide.

When crystallized from water, it melts in its water of crystallization at 143.2–144.2°C. (cor.), solidifies, and melts again at 177.8–178.8° (cor.). When dried at 190°C., it does not melt, but decomposes at 326.9–332.2° (cor.).

Analysis. 0.1428 gram sample gave 0.0096 gram BeO; 0.2474 gram sample gave 0.3042 gram $BaSO_4$; 0.2078 gram sample lost 0.0400 gram water. Calculated: BeO, 6.62; S, 16.90; H_2O, 19.20. Found: BeO, 6.72; S, 16.89; H_2O, 19.25.

Beryllium 2-chlorotoluene-5-sulfonate

$[C_6H_3(CH_3)(Cl)SO_3]_2Be$

Beryllium 2-chlorotoluene-5-sulfonate is the only one of the sulfonates which does not melt, and yet a few crystals were once obtained which did melt in their water of crystallization. A detailed study was not made, but it would appear that crystallization under different conditions might produce different hydrates. The crystals do not melt even if the melting point tube is sealed and suddenly immersed in the sulfuric acid bath every ten degrees, and yet they lose weight when heated in an oven at 190–200°C.

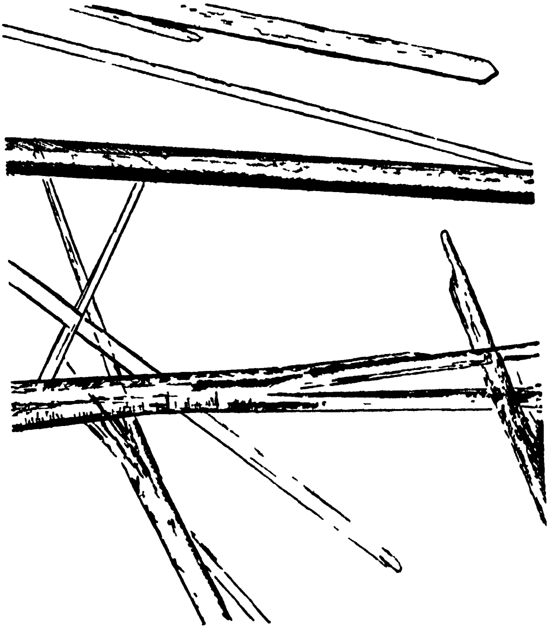


FIG. 3. BERYLLIUM 2-CHLOROTOLUENE-5-SULFONATE

The salt may be boiled to dryness without much hydrolysis. It crystallizes from a mixture of dry acetone and carbon tetrachloride in long, colorless needles which are apparently monoclinic, since they have an extinction angle of 4° in one position, and show parallel extinction in the other two.

Beryllium 2-chlorotoluene-5-sulfonate is very soluble in water, absolute alcohol, hot glacial acetic acid, and acetone, and insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane.

It decomposes at 384.7–399.7°C. (cor.).

Analysis. (1) 0.2964 gram gave 0.0178 gram BeO and 0.3378 gram $BaSO_4$. Calculated: BeO, 5.97; S, 15.26. Found: BeO, 6.01; S, 15.65.

(2) 0.2514 gram gave 0.0158 gram BeO and 0.2814 gram $BaSO_4$. Calculated: BeO, 5.97; S, 15.26. Found: BeO, 6.29; S, 15.37. Molecular weight: calculated, 420.24; found 440.3,418.0.

Beryllium benzenesulfonate

$(C_6H_5SO_3)_2Be$

The barium salt used in the preparation of beryllium benzenesulfonate was not made from the acid because it was not available. Instead, a mixture of benzene sulfochloride and water was boiled, barium hydroxide being added slowly, until, after boiling a few minutes, the solution no longer became acid. The solution was then filtered by suction, the barium benzenesulfonate immediately crystallizing out in colorless plates, apparently triclinic, showing brilliant polarization colors under the microscope.

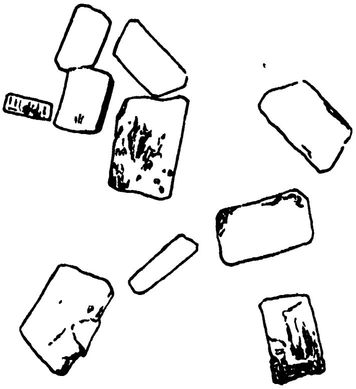


FIG. 4. BERYLLIUM BENZENESULFONATE

Beryllium benzenesulfonate was made by double decomposition in the usual way. If the solution is evaporated on a water-bath, a hard solid results, which contains water of crystallization. This cannot be entirely removed by drying in an oven because the salt decomposes. After drying at about 120°C., the salt was cooled in a desiccator, pulverized, and recrystallized from a mixture of acetone and chloroform. The product gave no test for chlorides, even though there was a large amount mixed with the crude salt.

Beryllium benzenesulfonate crystallizes from water in monoclinic plates having an extinction angle of 6° in one position and showing parallel extinction in the other two. These crystals appear to contain more water of crystallization than those recrystallized from a mixture of acetone and chloroform. The latter seem to be deliquescent.

Beryllium benzenesulfonate is very soluble in water, glacial acetic acid, alcohol, and acetone. It is insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, and dichloromethane. It seems to be very slightly soluble in hot chloroform.

When crystallized from a mixture of acetone and chloroform, the salt melts in its water of crystallization at 72.9–74.9°C. (cor.), and again at 94.4°C. (cor.), but if dried in the oven at 90–100°C., it melts only at 94.4°C. If it is carefully dried in the oven in a capillary tube, the temperature being slowly raised to 190°C., it does not melt. It begins to decompose at 358.7°C. (cor.).

For analysis, the samples were placed in small tubes and carefully dried to constant weight at 120–130°C. Some samples seemed to lose all their water at this temperature, but others decomposed, or else still contained water.

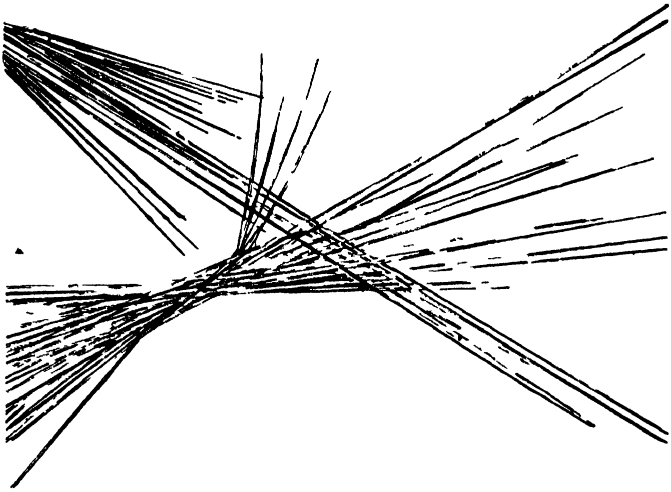


FIG. 5. BERYLLIUM 2-NITROTOLUENE-4-SULFONATE

Analysis. Calculated: BeO, 7 71. Found: BeO, 7.76.

Beryllium 2-nitrotoluene-4-sulfonate

$[C_6H_3(CH_3)(NO_2)SO_3]_2Be$

The barium salt used in the preparation of beryllium 2-nitrotoluene-4-sulfonate was also made by hydrolysis of the sulfochloride, instead of by neutralizing the free acid. It crystallizes from water solution in large yellow plates, which seem to be triclinic and show brilliant polarization colors.

The beryllium salt was made in the usual way, and recrystallized from a mixture of acetone and toluene. The salt crystallizes from this solution in monoclinic needles having an extinction angle of 6° in one position and showing parallel extinction in the other two. They exhibit polarization colors.

Beryllium 2-nitrotoluene-2-sulfonate is very soluble in water, absolute alcohol, acetone, and glacial acetic acid, and insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane. It appears to be slightly hygroscopic.

When crystallized from a mixture of acetone and toluene, it melts in its water of crystallization at 140.6 –141.6°C. (cor.), then solidifies, and melts again at 181.3–182.3°C. (cor.). If carefully dried in an oven at 160°C., it does not melt, but decomposition is noticeable at 273.6°C. (cor,).

Analysis. Calculated: BeO, 5.69; S, 14.53. Found: BeO, 6.05; S, 14.85.

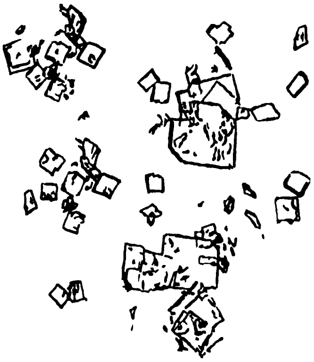


FIG. 6. BERYLLIUM *m*-NITROBENZENESULFONATE

Beryllium m-nitrobenzenesulfonate

$[C_6H_4(NO_2)SO_3]_2Be$

Beryllium *m*-nitrobenzenesulfonate was made in the usual way. The water solution cannot be evaporated to dryness over a flame without decomposition. After evaporation in a vacuum desiccator, it was carefully dried in an oven and recrystallized from a mixture of acetone and carbon tetrachloride. It is hygroscopic.

The crystal system of the salt when crystallized from a mixture of acetone and carbon tetrachloride was not determined, but the crystals forming on a slide as the solvent evaporated were monoclinic, having an extinction angle of 7° in one position and showing parallel extinction in the other two.

Beryllium *m*-nitrobenzenesulfonate is very soluble in water, absolute alcohol, acetone, and hot glacial acetic acid. It is insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane.

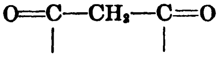
When crystallized from a mixture of acetone and carbon tetrachloride, it melts in its water of crystallization at 146.8°C. (cor). If dried at 180°C., it melts at 203.7–204.7°C. (cor.). It does not solidify on further heating, but begins to decompose at 231.8°C. (cor.).

Analysis: Calculated: BeO, 6.07. Found: BeO, 5.95.

Part II

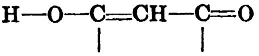
CHELATE BERYLLIUM COMPOUNDS

In striking contrast to the beryllium salts of organic acids, beryllium acetylacetonate is a well-defined chemical compound (8). It is the product formed by replacing one hydrogen atom of each of two molecules of acetylacetone by one atom of beryllium, and is one of a series of metallic salts of tautomeric enol-keto compounds, the so-called chelate compounds. The replaceable hydrogen atoms in the keto-form (9) are attached to a carbon atom which is between two carbonyl groups,



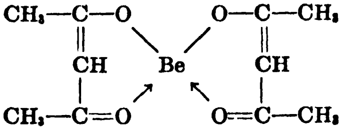
$$O{=}C{-}CH_2{-}C{=}O$$

The enol form, which forms salts, is



$$H{-}O{-}C{=}CH{-}C{=}O$$

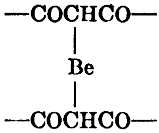
Or, as Sidgwick states, in beryllium acetylacetonate there are "rings with one definite coördinate link, in which the metallic (or hydrogen) atom is joined to the ring on one side by a normal link, and on the other by a coördinate link,



Chelate rings of this type are very stable. Such compounds have very different properties from the ordinary salts of organic acids; for instance, they are soluble in most organic solvents and practically insoluble in water. The possibility of their being of use as solutes for the electrodeposition of beryllium and in other ways led to the second part of this work—the preparation of a few beryllium salts of such compounds.

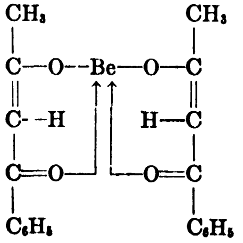
The copper salts of these compounds have been the most investigated. They are usually made by shaking an alcoholic solution of the ketone or ester or its sodium salt with copper acetate or sulfate, often with the addition of ammonia. If chlorides are used an addition product, consisting of the copper salt and the metallic chloride or hydrogen chloride, is formed. The copper salts, as well as those of most metals, are crystalline and insoluble in water and ether, but are easily recrystallized from hot alcohol, benzene, or chloroform. Although it is possible to make the beryllium salts in this way, it is not desirable, because the product is generally very impure, owing to the insolubility of beryllium hydroxide or carbonate in the ketone or ester used. Therefore a different procedure was followed in each case, according to the solubilities of the raw materials and products.

Two ketones, benzoylacetone, $C_6H_5COCH_2COCH_3$, and dibenzoylmethane, $C_6H_5COCH_2COC_6H_5$ and one ester, ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$, were chosen as typical enol-keto compounds from which to make beryllium salts, in order to find out whether their properties resemble those of beryllium acetylacetonate. Each contains the grouping



$$\begin{array}{c}\text{—COCHCO—}\\ | \\ \mathrm{Be} \\ | \\ \text{—COCHCO—}\end{array}$$

Beryllium benzoylacetonate



Enol form

We first tried to prepare beryllium benzoylacetonate by a method similar to that used by Combes (11). An alcoholic solution of benzoylacetone[4] was added to moist freshly precipitated beryllium hydroxide, to which a little absolute alcohol had been added. Since the benzoylacetone is very insoluble in water, it immediately precipitates, along with the beryllium benzoylacetonate. The latter may be separated from the excess beryllium hydroxide by extraction with chloroform, but, since this also dissolves the benzoylacetone, the product is very impure. However, the two may be separated by alcohol in which the salt is not very soluble, whereas the ketone is very soluble. The yield is very poor.

[4] The benzoylacetone was made according to Vanino, Präparative Chemie, Band 2, p. 537.

We found that the salt also may be made by allowing beryllium sulfate to stand in an alcohol solution of benzoylacetone, but this too is a poor method, yielding a mixture.

The best method we found was to add a weighed amount of beryllium nitrate dissolved in as little absolute alcohol as possible, drop by drop, to an equivalent weight of benzoylacetone also dissolved in as small a quantity of alcohol as possible, because the salt is soluble enough not to precipitate if the solutions are too dilute.[5] The crystals were washed with absolute alcohol to remove the mother liquor and any excess benzoylacetone, which is very soluble in alcohol. They were then stirred with water to remove any beryllium nitrate or nitric acid, again washed with alcohol, and then ether, and recrystallized from pure toluene or benzene. Large crystals may be obtained after a little practice. The temperature must be allowed to drop very slowly or else small crystals separate out even at 70°C. A small beaker containing the boiling toluene solution was placed in a boiling water-bath and the temperature of the latter was allowed to fall 20° every three hours. The solution was seeded at 75°C. At 55°C. the temperature was kept constant for two hours and then allowed to drop slowly to room temperature. Even then small crystals separated on filtering. The crystals were filtered immediately and washed with absolute alcohol and dry, fat-free ether. Large, perfect crystals may be obtained by allowing a benzene solution to evaporate, but on exposure to the air, these apparently lose benzene, becoming a white powder. Those crystallized

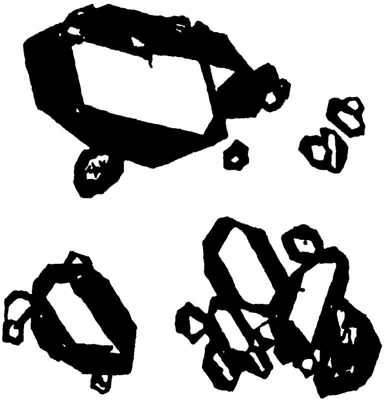


FIG. 7. BERYLLIUM BENZOYLACETONATE

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[5] In the latter case, crystals will sometimes form on standing, but usually the salt decomposes, yielding a brown oil. The crystals formed on standing are yellow, but if immediately precipitated, the product is nearly white. Considerably more of the salt may be recovered from the filtrate by evaporation under reduced pressure at 50–60°C.

from toluene do not change. They have the same melting point as the white powder left after the benzene evaporates from the other crystals. This would seem to indicate that they contain no toluene.

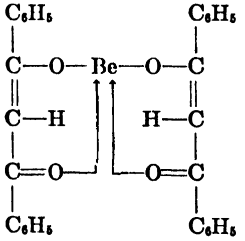
The crystals are highly refractive and show brilliant polarization colors. They show neither pleochroism nor absorption. They are monoclinic, having an extinction angle of 15° in one position and showing parallel extinction in the other two.

Beryllium benzoylacetonate is insoluble in water, almost insoluble in ether, fairly soluble in alcohol, benzene, carbon tetrachloride, toluene, and hot carbon disulfide, and very soluble in chloroform, acetone, and dichloromethane. It is insoluble in cold, but very soluble in hot glacial acetic acid. It is very slightly soluble in liquid ammonia. Ammonium hydroxide will not precipitate beryllium hydroxide, because the salt is insoluble in water, even if boiled seven hours, but if it is first boiled with nitric acid, and then made slightly alkaline with ammonium hydroxide, a heavy gelatinous precipitate results. It is very soluble in cold, concentrated sulfuric and nitric acids, and it dissolves in cold, concentrated hydrochloric acid on standing twenty-four hours. It is hydrolyzed by refluxing with dilute (1:4) nitric acid in half an hour, and dissolves in dilute hydrochloric and sulfuric acids after boiling four hours.

The crystals melt sharply at 210.2–211.2°C. (cor.), and begin to decompose noticeably at 224.8°C. (cor.). They may be sublimed if heated quickly, before they have time to melt.

Analysis. Calculated: BeO, 7.58. Found: BeO, 7.69, 7.65. Molecular weight: calculated, 331.24; found, 327.45, 343.6.

Beryllium dibenzoylmethane



Dibenzoylmethane was made by condensing ethyl benzoate with acetophenone by means of sodium and extracting the resulting sodium salt with a mixture of ice cold water and ligroin. The dibenzoylmethane was separated by adding acetic acid to the solution of the sodium salt, filtering, and recrystallizing from methyl alcohol. This method is exceedingly tedious, and gives a very small yield, because the sodium salt hydrolyzes easily, producing a brown oil (probably acetophenone or a derivative), which clogs the filter paper and cannot be separated from the product even by recrystallization. We found that a much quicker, easier way is to allow the ethyl benzoate, acetophenone, and sodium mixture to stand four or five days for the reaction to become complete, because a red-brown substance coats the sodium, making the reaction very slow. The resulting sodium salt was then washed with ether alone until it became nearly white, and dried in the air. The product was dissolved in water, and filtered quickly because it hydrolyzes easily. For the same reason it cannot be heated to get it into solution. The ketone was precipitated from this solution with acetic acid, at once. The crystals were collected on a filter, washed with water until a flame test showed only a trace of sodium, and allowed to dry in the air. The yield was fairly good, and the product almost white, although the melting point indicated that it was not pure.

The beryllium salt[6] was made by mixing equivalent amounts of the ketone and beryllium nitrate in absolute alcohol. The solutions must be made with as little alcohol as possible, because otherwise the crystallization is very slow, and the crystals impure. A warm solution of beryllium nitrate was added drop by drop to a warm solution of dibenzoylmethane. As soon as all the beryllium nitrate was added, and not before, needles of the beryllium salt began to separate[7] until the solution became almost solid. The crystals were filtered, washed with alcohol and ether and recrystallized from absolute alcohol. Since the salt is not very soluble, this is a slow process. It crystallizes in long, pale yellow needles, which are pure. The crystals are light and mat easily. They do not stick together, but adhere to everything else, so that it is practically impossible to make pellets of them for a molecular weight determination. They cannot be introduced into the tube by a paper funnel because they stick to the paper. If the salt is put into small glass tubes and then slid into a larger tube, it does not dissolve completely out of the tubes even if allowed to boil all day. Therefore a molecular weight determination was not made.

The needles show brilliant polarization colors and are apparently monoclinic, having an extinction angle of 5° in one position and showing parallel extinction in the other two. The ends are always jagged, as no pinacoid or prism faces form. (See figure 8, page 75.)

Beryllium dibenzoylmethane is insoluble in water, slightly soluble in ether, fairly soluble in carbon tetrachloride, toluene, and hot alcohol, and very soluble in benzene, chloroform, acetone, carbon disulfide, and dichloromethane. It is insoluble in cold glacial acetic acid, but very soluble when heated. It is insoluble in liquid ammonia.

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[6] It cannot be made by mixing the ketone with beryllium hydroxide because the ketone, being insoluble in water, precipitates immediately, along with what little of the salt is formed.

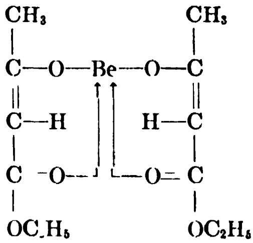
[7] If the materials are not in equivalent amounts, or if the dibenzoylmethane is not almost white, no crystals separate. If it stands long enough, or is distilled under reduced pressure, a brown paste results which cannot be easily purified. A very small amount may be recovered by leaching out the impurity with alcohol, in which beryllium dibenzoylmethane is not very soluble. If the dibenzoylmethane is pure, a good deal of the product may be recovered from the filtrate by evaporation under reduced pressure.

Beryllium hydroxide is not precipitated on addition of ammonium hydroxide to a mixture of the salt and water, owing to the insolubility of the salt, but after it is boiled a few minutes with nitric acid, ammonia causes a heavy gelatinous precipitate. It is neither dissolved nor hydrolyzed by water, even after seven hours boiling. It is very soluble in cold concentrated sulfuric acid and nitric acid. It does not dissolve in cold, concentrated hydrochloric acid, but dissolves when heated. It is insoluble in dilute sulfuric acid and hydrochloric acid, even when boiled seven hours. After two hours boiling, it dissolves in dilute nitric acid, with the separation of a white, powdery precipitate.

The crystals melt sharply at 214–215°C. (cor.), and do not decompose easily. A noticeable change in color occurred at 262° (cor.). The compound may be sublimed if heated quickly, before it melts.

Analysis. Calculated: BeO, 5.51. Found: BeO, 5.60.

Beryllium ethyl acetoacetate



Beryllium ethyl acetoacetate was prepared by stirring ethyl acetoacetate into moist beryllium hydroxide to which a little absolute alcohol had been added. As soon as the acetate was added, a salmon-pink oil began to separate. The reaction must be watched, because if allowed to stand too long, the mixture becomes a mass of crystals which cannot be separated from the excess beryllium hydroxide. The reaction may be complete in one hour or may take several days. The beryllium ethyl acetoacetate cannot be separated by extraction with ether, because some ethyl acetoacetate is dissolved also, contaminating the product. Therefore small portions of the oil were removed by a pipet about every five minutes and dropped into ice-cold distilled water. When a sample formed crystals immediately, the oil was quickly separated from the beryllium hydroxide by a pipet. The oil was separated by a suction filter from any beryllium oxide which might have been included and poured into about twenty times its own volume of ice-cold distilled water. The beaker was packed in ice and left until the oil had entirely solidified. If left in the water too long, the salt hydrolyzes. Since the crystals are light, they leave the oil and rise to the surface. As soon as this happened, the mass was separated from the liquid on a suction filter. The crystals were removed from the funnel and stirred with 400–600 cc. of distilled water at room temperature, and again filtered. The washing was repeated until the product was pure white. It must be done quickly in order to prevent hydrolysis. Dried in a vacuum desiccator, the salt becomes a pure white, fluffy, crystalline product which melts sharply at 60.6°C., giving a clear melt. It is too soluble in most organic solvents to be easily recrystallized. The product may be separated from any beryllium oxide by dissolving in fat-free ether and filtering. Since crystals do not form until the ether has evaporated, a photograph of the separate crystals is difficult to obtain. As the ether evaporates, crystals build up on the edges of the filter paper, and these were scraped off and photographed.

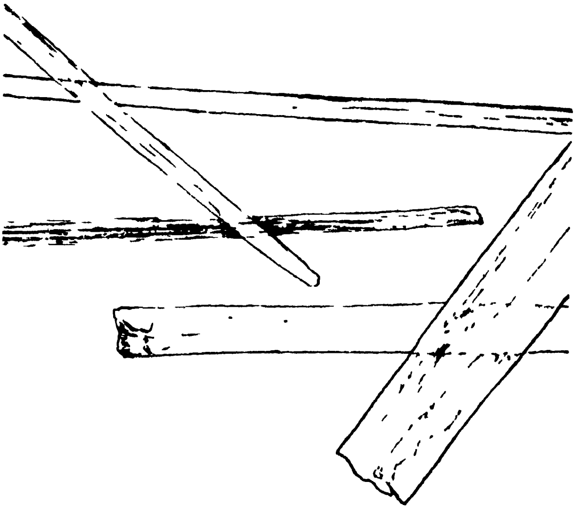


FIG. 8. BERYLLIUM DIBENZOYLMETHANE

Owing to the fact that the crystals could not be separated from the mother liquor, it was difficult to determine the crystal system to which they belong. They seem to be monoclinic, having an extinction angle of 7° in one position and showing parallel extinction in the other two.

Beryllium ethyl acetoacetate is insoluble in water and very soluble in alcohol, ether, benzene, carbon tetrachloride, dichloromethane, and glacial acetic acid. It is only slightly soluble in liquid ammonia contained in an open beaker. It begins to decompose into beryllium hydroxide and ethyl acetoacetate if allowed to stand in water a few moments, and hydrolysis is complete on boiling. It dissolves instantly in cold concentrated hydrochloric acid, in nitric acid, and in dilute sulfuric acid. In the latter case, an oil separates. Beryllium ethyl acetoacetate is very soluble in cold, concentrated sulfuric acid, in dilute hydrochloric acid, and in dilute nitric acid.

It melts sharply at 60.6–61.1°C. (cor.), giving a clear melt. If heated slowly, it begins to decompose at 228.5°C. (cor.), turning yellow.

Since the most carefully made salt still contained about 7 per cent of beryllium oxide, which was the only impurity provided the washing was thorough, this had to be removed before analysis. A pure product was obtained by dissolving the impure salt in dry, fat-free ether, filtering, and driving off the ether on a water-bath. The melted salt was then poured into a weighed glass tube; such as is used in Carius analyses, and cooled in a desiccator and analyzed.

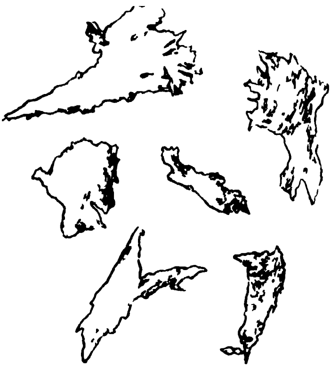


FIG. 9. BERYLLIUM ETHYL ACETOACETATE

Analysis. Calculated: BeO, 9.39. Found: BeO, 9.52, 9.46. Molecular weight: calculated, 267.24; found, 266.8, 261.2.

After this work was finished, an article (13) appeared describing the preparation of beryllium ethyl acetoacetate by a slightly different method from that by which it was prepared in this laboratory. "Beryllium acetoacetic ester was prepared according to the method described by Konrad (Ann. **188,** 273) for the preparation of the aluminum compound. A berylate solution was prepared by adding strong potassium hydroxide to 10.1 grams of beryllium sulfate until the alkali was slightly in excess, and then adding 17 grams of freshly distilled acetoacetic ester. From the originally clear solution, there soon separated colorless leaflets, which could be recrystallized from petroleum ether, and which melted at 63°C. The yield was 3 grams, 20 per cent of the theoretical. The crystals may be easily distilled in a vacuum at 166°C. under a pressure of 13 mm. They are readily soluble in alcohol, benzene, etc."

SUMMARY OF PART II

Beryllium benzoylacetonate and beryllium dibenzoylmethane were found to be very similar to beryllium acetylacetonate. They are both crystalline, well-defined compounds, soluble in alcohol, acetone, chloroform, benzene, carbon tetrachloride, toluene, carbon disulfide, and dichloromethane, and insoluble in water. They melt sharply, but at much higher temperatures than the acetylacetonate, 210.2°C. and 214°C., respectively, and they do not sublime readily, although they may be sublimed if heated quickly, before they have time to melt; beryllium acetylacetonate melts at 108°C. and begins to sublime even before 100°C. They are soluble in concentrated acids, but are not hydrolyzed by water even after boiling seven hours.

Beryllium ethyl acetoacetate, however, although it dissolves in the same solvents, is much too soluble to be crystallized from any of them. It is very easily hydrolyzed to beryllium hydroxide and ethyl acetoacetate, even in cold water. Hydrolysis also takes place when toluene, benzene, or ether solutions are allowed to evaporate slowly and is probably due to water absorbed by solvent. Beryllium ethyl acetoacetate melts at a much lower temperature than the other two compounds, namely, 60.6°C. It may be sublimed if heated quickly under reduced pressure, but under atmospheric pressure it melts, and, if carefully heated, may be distilled at about 150°C., although some decomposition always takes place.

A comparison of the solubilities of the salts in ether is interesting. Beryllium ethyl acetoacetate is exceedingly soluble; beryllium acetylacetonate is soluble; beryllium dibenzoylmethane is slightly soluble; while beryllium benzoylacetonate is almost insoluble.

SUMMARY

The following compounds have been made and analyzed, and their properties studied: beryllium *p*-toluenesulfonate, beryllium *p*-xylenesulfonate, beryllium 2-chlorotoluene-5-sulfonate, beryllium benzenesulfonate, beryllium 2-nitrotoluenesulfonate, beryllium *m*-nitrobenzenesulfonate, beryllium benzoylacetonate, beryllium dibenzoylmethane, and beryllium ethyl acetoacetate.

REFERENCES

(1) Parsons: The Chemistry and Literature of Beryllium, p. 71. The Chemical Publishing Co., Easton, Pa. (1909).
(2) Parsons: J. Am. Chem. Soc. **31**, 1205 (1909).
(3) Parsons: J. Phys. Chem. **11**, 659 (1907).
(4) Sidgwick and Lewis: J. Chem. Soc. **129**, 1287 (1926).

(5) Reference 1, p 17

(6) Booth and Torrey J Phys Chem **35**. 2468 (1931)

(7) Reference 1, p 69

(8) Parsons J Am Chem Soc **26**, 732 (1904)

(9) Sidgwick The Electronic Theory of Valency, p 240 Oxford University Press, London (1929)

(10) Morgan J Chem Soc **T105**, 189 (1914); **T117**, 1457 (1920) for a discussion of the structure of these compounds

(11) Combes Compt rend **119**, 1221 (1894)

(12) Vanino Praparative Chemie, Zweite Auflage, Band 2, Organische Teil, p 538.

(13) Weygand and Forkel Ber **59**, 2246 7 (1926)

THE ELECTRICAL CONDUCTIVITY OF MIXED SALT SOLUTIONS[1]

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An examination of the literature shows that few experimental studies have been made on the electrical conductivity of systematic mixtures of electrolytes. Two recent papers that do contribute directly to this subject are by Stern (1) and Ruby and Kawai (2). Stern examined the equivalent conductivity of systematic mixtures of the sodium and potassium halides from 0.1 *M* to 4 *M* at 25°C. He compared his experimental values with values calculated on the assumption that the conductivity of the mixture is additive. He did not find this rule to hold true. Ruby and Kawai studied the various combinations of sodium chloride, potassium chloride, and hydrochloric acid for the purpose of "discovering the nature of such solutions and to test the value of the methods of calculating the conductances of solutions of such mixtures of electrolytes." They did not find their experimental values to fit into any of the known methods for calculating such data. In addition to these two papers, H. C. Jones and C. M. Stine (3) worked with a variety of salt mixtures but their concentrations, with few exceptions, did not go below 0.5 *N*. Pascoe (4) worked with mixed salt solution in an attempt to correlate the conductivity of plant saps and of soils with their ionic concentrations. The present investigation was undertaken for the purpose of extending such conductivity data over a wider range of salts and into higher valence types in the hope of revealing the factor or factors that are responsible for their erratic behavior.

MATERIALS

The salts used in this investigation, namely, sodium chloride, sodium sulfate, magnesium chloride, magnesium sulfate, copper sulfate, zinc sulfate and potassium chloride, and the hydrochloric acid used were all of a C.P. grade and no further purification was attempted except for the magnesium sulfate, which was recrystallized once, and the hydrochloric acid, which was redistilled. The sodium chloride, potassium chloride, and sodium sulfate solutions were prepared by direct weighing of the dried salt; the hydrochloric acid was standardized according to the method of Hulett and Bonner (5); the other solutions were prepared by precipitating the sulfates as barium sulfate and the chlorides as silver chloride and weighing the respective precipitates. In general, the dilute solutions were prepared from the more concentrated ones. Double-distilled water was used in the preparation of the solutions that had a specific resistance of approximately 5 × 10^{-6} mhos and the solutions were preserved in Pyrex glass. The solutions were volume normal at 20°C. and burettes were used in proportioning them in the combinations desired. The combinations copper sulfate–sodium chloride, zinc sulfate-sodium chloride, sodium sulfate-sodium chloride, and magnesium sulfate–magnesium chloride were studied at 0.01 *N*, 0.1 *N*, 1 *N*, and 2 *N* concentrations; the other combinations did not cover as wide a range of concentration.

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[2] Guest of the University of Minnesota.

APPARATUS AND PROCEDURE

The usual Wheatstone bridge set-up was used in making the conductivity measurements, consisting of a Leeds and Northrup precision bridge with extension coil, a Leeds and Northrup precision resistance box, a type E Vreeland Oscillator at 1000 cycles, a telephone tuned to 1000 cycles, and three conductivity cells of the Washburn (6) type. The cell constants were 2.544, 17.11, and 115.0. Since most of the measurements were made during the warm part of the summer, a higher temperature than usual was used in this work, namely 30.17°C. ±0.02. The ratio of the bridge arms was determined and suitable corrections made in the calculations. The water correction was made in the solutions of 0.01 *N* concentration. All glassware was standardized and corrections were made, where necessary.

RESULTS

The results are given in table 1, which includes the names of the combinations studied, the proportion of each compound in the mixture, the experimental values and $\Delta\Lambda$, the difference between the experimental value and that calculated on the assumption that the conductance of the mixture is additive. $\Delta\Lambda$ is given a positive sign when the calculated value is greater than the observed value, and a negative sign when less than the observed value.

DISCUSSION

The data presented here do not show any decided regularity in their behavior. Such combinations as copper sulfate–sodium chloride, zinc sulfate–sodium chloride, sodium sulfate–sodium chloride, and potassium

TABLE 1

Conductivity data and ΔΛ, the difference between the calculated and experimental values

T = 30 17°C.

CONCENTRATION OF SOLUTION								
NaCl $CuSO_4$	0 0100 *N* 0 0100 *N*		0 1000 *N* 0 1000 *N*		1 000 *N* 0 9295 *N*		2 000 *N* 1 859 *N*	
VOLUME OF SOLUTION Ratio NaCl $CuSO_4$	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	131 2		119 0		95 50		83 30	
80.20	127 1	−4 0	110 1	−3 9	83 82	−0 71	71 20	0 87
60.40	121 0	−5 9	98 41	−5 0	71 55	−0 83	59 44	1 40
50.50	116 6	−5 6	91 50	−4 5	65 18	−0 65	53 86	1 36
40.60	111 8	−4 8	84 87	−4 3	59 00	−0 67	48 19	1 41
20 80	101 5	−2 6	70 47	−2 7	46 40	−0 46	37 53	0 84
0.100	90 87		55 01		33 55		27 14	

T = 30 17°C.

CONCENTRATION OF SOLUTION								
NaCl $ZnSO_4$	0 0100 *N* 0 0100 *N*		0 1000 *N* 0 1000 *N*		1 000 *N* 1 000 *N*		2 000 *N* 1 859 *N*	
VOLUME OF SOLUTION Ratio NaCl $ZnSO_4$	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	130 9		118 9		95 52		83 32	
80.20	128 2	−4 5	110 5	−3 7	82 61	0 52	68 39	3 61
60.40	121 7	−5 5	99 32	−4 5	70 38	0 60	57 49	3 20
50:50	117 7	−5 1	93 70	−4 9	64 21	0 54	52 60	2 43
40·60	114 0	−5 1	87 80	−5 1	58 20	0 31	47 49	1 88
20 80	104 8	−3 3	73 52	−2 9	46 00	0 04	37 35	0 71
0:100	94 21		58 60		33 57		26 74	

T = 30 17°C

CONCENTRATION OF SOLUTION								
NaCl Na_2SO_4	0 0100 *N* 0 0100 *N*		0 1000 *N* 0 1000 *N*		1 000 *N* 1 000 *N*		2 000 *N* 2 000 *N*	
VOLUME OF SOLUTION Ratio NaCl Na_2SO_4	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	131 0		118 9		95 52		82 09	
80:20	129 9	−0 1	115 5	−0 2	88 34	0 29	75 39	0 75
60:40	128 9	−0 3	111 9	−0 3	82 29	1 45	68 98	1 22
50:50	128 4	−0 3	109 9	−0 1	79 58	1 21	65 98	1 25
40:60	127 7	−0 2	107 8	0 2	76 69	1 15	62 97	1 28
20:80	126 4	−0 1	104 2	0 1	71 32	0 63	57 56	0 75
0:100	125 1		100 7		66 06		52 36	

TABLE 1—*Continued*

T = 30 17°C.

CONCENTRATION OF SOLUTION								
$MgCl_2$	0 0093 N		0 0927 N		0 9270 N		2 000 N	
Na_2SO_4	0 0093 N		0 0932 N		0 9315 N		2 000 N	
VOLUME OF SOLUTION Ratio $MgCl_2$ Na_2SO_4	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	127 4		110 9		80 85		64 38	
90:10			106 3	3 50	77 72	1 74		
80:20	121 8	5 0	103 3	5 41	75 39	2 67	59 78	2 2
70:30	120 1	6 4	101 1	6 51	71 94	4 73		
60:40	119 1	7 1	98 09	8 42	69 80	5 48	55 78	3 8
50:50	118 4	7 5	96 37	9 04	67 97	5 92	54 07	4 3
40:60	118 1	7 5	95 40	9 28	66 76	5 73	53 07	4 1
30:70	118 3	7 0	95 04	9 18	66 53	4 47		
20.80	120 4	4 6	96 57	5 55	66 00	3 71	52 02	2 7
10:90			98 16	2 87	66 43	1 88	52 16	1 4
0 100	124 4		99 93		66 92		52 36	

30 17°C.

CONCENTRATION OF SOLUTION						
$MgCl_2$	0 0100 N		0 0927 N		0 9270 N	
$MgSO_4$	0 0100 N		0 0930 N		0 9295 N	
VOLUME OF SOLUTION Ratio $MgCl_2$ $MgSO_4$	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	128 9		111 9		80 57	
90:10			105 5	1 66	75 96	0 34
80:20	121 1	1 7			71 60	0 43
70:30			95 70	1 97	66 99	0 68
60:40	115 0	1 7	90 85	2 08	62 17	1 23
50:50	112 0	1 7	86 18	2 01	58 06	1 17
40·60	109 2	1 4	81 78	1 67	53 58	1.38
30:70					49 52	1.17
20:80	103 5	1 1	72 59	1 37	45 45	0 98
10.90			68 59	0 63	41 52	0 64
0.100	98 46		64 48		37 89	

TABLE 1—*Continued*

T = 30 17°C

CONCENTRATION OF SOLUTION				
MgCl$_2$ NaCl	0 0927 *N* 0 1000 *N*		0 927 *N* 1 000 *N*	
VOLUME OF SOLUTION Ratio MgCl$_2$ NaCl	Λ	ΔΛ	Λ	ΔΛ
100 0	109 8		80 46	
90 10			81 89	−0 01
80 20	111 7	−0 1	83 56	−0 26
70 30			84 90	−0 18
60 40	114 1	−0 7	86 65	−0 41
50 50	114 9	−0 5	87 74	−0 17
40 60	116 0	−0 7	89 17	−0 25
20 80	117 8	−0 7	92 11	−0 27
10 90			93 57	−0 31
0 100	118 9		94 68	

CONCENTRATION OF SOLUTION				
KCl HCl	0 0100 *N* 0 0100 *N*		0 5000 *N* 0 5000 *N*	
VOLUME OF SOLUTION Ratio KCl HCl	Λ	ΔΛ	Λ	ΔΛ
100 0	156 2		128 2	
80 20	213 8	0 9	181 6	−0 2
60 40	272 1	1 0	234 5	0 0
50 50	301 5	0 9	261 5	−0 4
40 60	331 0	0 6	289 5	−1 8
20 80	390 0	0 0	341 7	−1 9
0 100	448 5		394 0	

T = 0°C

CONCENTRATION OF SOLUTION		
NaCl CuSO$_4$	0 1000 *N* 0 1000 *N*	
VOLUME OF SOLUTION Ratio NaCl CuSO$_4$	Λ	ΔΛ
100 0	58 28	
80 20	53 56	−1 47
60.40	47 43	−1 53
50 50	44 51	−1 71
40 60	41 30	−1 60
20 80	34 20	−0 69
0 100	27 32	

TABLE 1—*Concluded*

T = 30 17°C.

CONCENTRATION OF SOLUTION		
$CuSO_4$	0 0100 N	
$ZnSO_4$	0 0100 N	
VOLUME OF SOLUTION Ratio $CuSO_4$ $ZnSO_4$	Λ	$\Delta\Lambda$
100:0	90 55	
80:20	91 93	−0 66
60:40	92 62	−0 63
50:50	93 45	−1 09
40:60	93 66	−0 95
20:80	94 38	−0 94
0:100	94 16	

chloride–hydrochloric acid show positive, negative, and zero values for $\Delta\Lambda$; other combinations, such as magnesium chloride–sodium sulfate and magnesium chloride–magnesium sulfate, show only positive deviations for the concentrations studied. The results, as a whole, suggest, however, that when a sufficiently wide range of concentrations has been studied for any combination, they will show all three variations from the straight line curve. Table 2 is a tabulation of these deviations expressed qualitatively; the table also includes data taken from Stern (1) and from Ruby and Kawai (2). Our data are not strictly comparable with those of Stern and of Ruby and Kawai since they used weight-normal solutions, whereas we used volume-normal; the general trend of all three researches, however, is the same.

No explanation is offered at the present time for the apparently erratic behavior of these conductivity measurements. Stern used the theory of complex ion formation to explain his data; this requires a positive value for $\Delta\Lambda$ and that this value should increase with increasing concentration. Our measurements do not reasonably substantiate this theory, since all the $\Delta\Lambda$ values found for the combination magnesium chloride–sodium chloride are negative and likewise for the combination potassium chloride–hydrochloric acid at concentrations above 0.5 N. Even the combinations magnesium chloride–sodium sulfate and magnesium sulfate–magnesium chloride, which gave positive values for $\Delta\Lambda$ for all values studied, do not support the complex theory since the values at 0.1 N concentration are larger than at either higher or lower concentrations. If complex ions do occur in these solutions and contribute to the erratic behavior of their conductivities, then it is evident that their effect is less than some other superimposed phenomena.

In considering the problem of complex ions it should be kept in mind also that the studies of MacInnes (7), Dewey (8) and others on the transport numbers of the sodium and potassium halides have failed to find complex ions in these solutions.

The inter-ionic attraction theory of Debye and Hückel (9) and its modification by Onsager (10) in its present state cannot be applied to these data since it has been developed for systems containing only two ionic species. While Bennewitz, Wagner, and Küchler (11) have extended Onsager's calculations to ternary ion mixtures it is still inapplicable, since their method requires that one of the three ionic species shall be limited to a small concentration in comparison to the other two ions.

TABLE 2

Showing the direction of the deviation of the experimental from the calculated values

NORMAL CONCENTRATION	0.01	0.1	0.5	1	2	4
Combination:						
$CuSO_4$–NaCl	–	–		–	+	
$ZnSO_4$–NaCl	–	–		+	+	
$CuSO_4$–$ZnSO_4$	–					
Na_2SO_4–NaCl	–	–		+	+	
$MgCl_2$–Na_2SO_4	+	+		+	+	
$MgCl_2$–$MgSO_4$	+	+		+		
$MgCl_2$–NaCl		–		–		
KCl–HCl	+		–			
KCl–HCl*			+	–	–	–
NaCl–HCl*			+	+	+	–
KCl–NaCl*			–	+	+	+
KCl–NaCl†		–	+	+	+	+
KBr–NaBr†		–	+	+	+	+
KI–NaI†		–	+	+	+	+

Sign is negative when observed value is greater than calculated; positive the converse.

* Taken from Ruby and Kawai.

† Taken from Stern.

The effect of solvation of the ions on their electrical conductivity is without a doubt a factor of considerable magnitude, but accurate information on solvation is too limited to be of much satisfaction. Attention should be called, however, to the similarity of our curves with those obtained by Jones and collaborators (3) wherein they measured the conductivity of salts in mixed solvents. Their data, which they obtained by varying the ratio of the solvent components and keeping constant the concentration of the salt, give curves that have essentially the same characteristics as those obtained by us. This permits the conclusion that the reaction between the solute and the solvent is of major importance in the interpretation of electrical conductivity data.

REFERENCES

(1) Stearn, A. E.: J. Am. Chem. Soc. **44,** 670 (1922).
(2) Ruby, C. E., and Kawai, J.: J. Am. Chem. Soc. **48,** 1119 (1926).
(3) Jones, H. C., and Stine, C. M.: Carnegie Inst. Wash., Pub. No. 180 (1913).
(4) Pascoe, T. A.: M. S. Thesis, University of Minnesota (1926). Cited by R. A. Gortner in Outlines of Biochemistry, pp. 269–270. John Wiley and Sons, New York (1929).
(5) Hulett, G. A., and Bonner, W. D.: J. Am. Chem. Soc. **31,** 390 (1909).
(6) Washburn, E. W.: J. Am. Chem. Soc. **38,** 2431 (1916).
(7) MacInnes, D. A.: J. Am. Chem. Soc. **47,** 1922 (1925).
(8) Dewey, Jane: J. Am. Chem. Soc. **47,** 1927 (1925).
(9) Debye and Hückel: Physik. Z. **24,** 185 (1923); **24,** 305 (1923); Trans. Faraday Soc. **23,** 333 (1927).
(10) Onsager: Physik. Z **27,** 388 (1926); **28,** 277 (1927); Trans. Faraday Soc. **23,** 341 (1927).
(11) Bennewitz, Wagner, and Kuchler: Physik. Z. **30,** 623 (1929).

THE SYSTEM ETHYL ALCOHOL–*n*-HEPTANE AT 30°C.

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In the published account of their work, Smyth and Engel (1) draw attention to the curious results obtained for certain systems of which, perhaps, ethyl alcohol–*n*-heptane is the most important. They offered no adequate explanation for their observation that for certain solutions the partial pressures of alcohol exceeded the vapor pressure of pure alcohol at the same temperature. Although they searched for evidence, they found none to support the suggestion that the system might not be a true binary system of the components considered.

If this system is a true binary system of alcohol and *n*-heptane the results should agree with the equation of Duhem-Margules within the limits set by the deviations from the laws of perfect gaseous solutions on the part of the vapor, and this agreement would be independent of the complexity of the liquid phase. When their results are tested by this method, not only do the partial pressures of both components for solutions rich in alcohol appear to be at variance with this equation, but those for solutions rich in heptane also cannot be reconciled with it. A wide range of liquid compositions are involved and it seems unlikely that the assumption made in selecting the components could be the primary cause of the discrepancy. On the other hand, one would hesitate before attributing it to experimental error were it not for the fact that such errors have not infrequently affected the results of other careful workers in this field. For these reasons we undertook the study of the system by a method in which such errors as occurred would differ from those likely to occur in the Sameshima (2) method used by Smyth and Engel.

MATERIALS

We requested the Ethyl Gasoline Corporation to send us a sample of *n*-heptane identical in character with that used by Smyth and Engel. The heptane obtained from them was re-distilled. Our crude alcohol was anhydrous ethyl alcohol (Squibbs). This was dried with sodium, distilled in a carefully dried apparatus, and promptly transferred to dry glass capsules which were sealed off and later inserted into our apparatus proper.

METHOD AND RESULTS

The apparatus was identical with and the procedure similar to that used for the study of the system methyl alcohol-*n*-hexane (3). The measurements were made at 30°C., since we feared that at higher temperatures and consequently at higher pressures the vapor would be very abnormal. We assumed that the deviation of the apparent formula weight $\left(F' = \frac{WRT}{PV}\right)$ from normal (100.13) was proportional to the partial pressure of the heptane and that this was the only complication in which the vapor was involved which merited consideration.

TABLE 1

The apparent formula weight of n-heptane

	TEMPERATURE	VAPOR COMPOSITION WEIGHT PER CENT OF HEPTANE	TOTAL PRESSURE	CALCULATED FORMULA WEIGHT
	°C			
(1)	34 9	100	58 2	100 6
(2)	34 8	100	58 5	100 9
(3)	34 9	100	60 2	101.3
(4)	34 6	71 3	102 9	101.6

TABLE 2

Vapor pressure determinations at 30.0°C.

SUBSTANCE	VAPOR PRESSURE	OBSERVER AND REFERENCE
Ethyl alcohol	78 4	Freed and Morris
	78 2	Freed and Morris
	78 2	Smyth and Engel (1)
	78 06	Young (5)
	78 5	Regnault (6)
n-Heptane	58 4	Freed and Morris
	59 0	Freed and Morris
	58 2	Freed and Morris
	58 5	Freed and Morris
	58 2	Smyth and Engel (1)
	58 35	Young (5)
Water	32 0	Freed and Morris
	31 8	International Critical Tables (4)

Several experiments were carried out in order to determine a suitable value for the apparent formula weight of *n*-heptane vapor at 58.4 mm. and 35°C. The results of these are given in table 1. It may be noted that the highest value was obtained in the last experiment. This suggests a slight volume change on mixing the pure vapors and this point will be further investigated by us. However, at these low pressures an exact determination could not be made and we chose as a probable value 101.0.

Although our previous investigations indicate the method of study to be an adequate one, this is no check on the manner in which the present work was performed. To some extent, the vapor pressure measurements given in table 2 constitute such a check.

TABLE 3

The coexistent phases, the total and partial pressures at 30.00 ±.01°C.

NUMBER	FORMULA WEIGHT OF n-HEPTANE	WEIGHT PER CENT OF ALCOHOL		TOTAL PRESSURE	CALCULATIONS BASED UPON WEIGHT PER CENT RESULTS AND THE FORMULA WEIGHTS 46.05 AND 101.0			
					Mole per cent of alcohol		Partial pressures	
		Liquid	Vapor		Liquid	Vapor	Alcohol	n-Heptane
1		100.0	100.0	78.3	100.0	100.0	78.3	0.0
2	100.3	92.7	67.2	94.3	96.5	81.8	77.1	17.2
3	100.6	82.0	48.9	110.0	90.8	67.7	74.5	35.5
4	100.9	67.7	40.5	119.4	82.2	59.9	71.5	47.9
5	100.9	47.2	37.7	122.0	66.3	57.1	69.6	52.4
6	100.9	19.4	36.0	122.0	34.6	55.2	67.4	54.6
7	101.0	13.5	35.1	120.5	25.5	54.2	65.3	55.3
8	101.0	5.7	31.5	115.2	11.7	50.2	57.8	57.4
9	101.0	5.1	32.3	117.1	10.5	51.2	59.9	57.2
10	101.0	2.2	28.9	109.0	4.7	47.2	51.4	57.6
11	101.0	0.6	22.9	95.0	1.4	39.5	37.5	57.5
12	101.0		16.7	83.5		30.5	25.5	58.1
13	101.0	0.0	0.0	58.4	0.0	0.0	0.0	58.4

Our results for the two component system are given in table 3. The liquid composition for No. 11 is not given. It was too close to pure heptane for accurate determination nor can it be better obtained from the total pressure curve by interpolation. A probable value of 0.5 mole per cent alcohol might be tentatively assigned. No. 8 was our first experiment with systems of low alcoholic content and is in our belief a poor determination. It is included because we do not wish to present selected results.

The total and partial pressures (No. 8 omitted) are indicated in figure 1. For comparison, the results of Smyth and Engel were recalculated to a basis of 101.0 for heptane and are also included. This recalculation did not materially alter the nature of their results. When one considers the actual differences between the two total pressure curves, it would appear that the curves are in fair agreement except at the heptane end. Thus their maximum pressure is 119.9 mm. whereas ours is 122 mm. On the

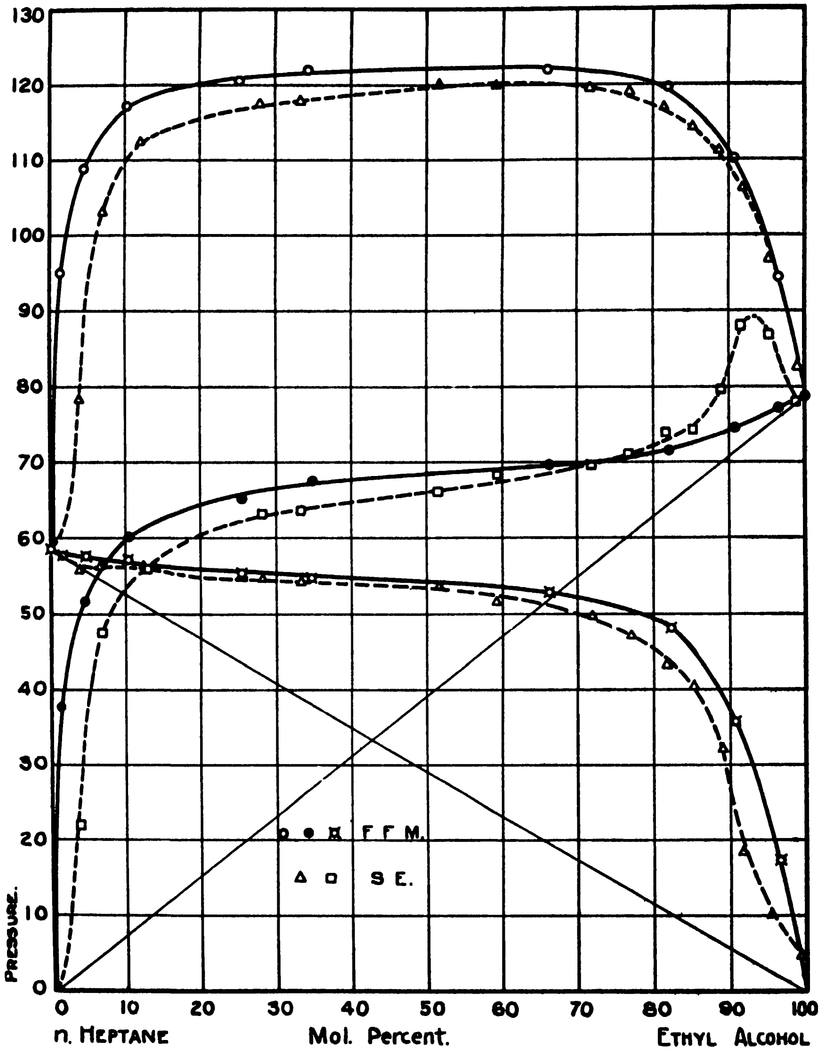

Fig. 1. Partial Pressures and Vapor Pressures

other hand, there are marked differences between our partial pressure curves. We found no evidence of points of inflection on these curves at their lower ends nor a maximum on the alcohol curve; in other words, no evidence of those peculiarities which were so markedly at variance with the equation of Duhem-Margules and which first excited our interest in this system.

SUMMARY

1. The compositions of the co-existent phases have been determined at 30.00°C. for the system ethyl alcohol-*n*-heptane.

2. The total pressures have been measured and the partial pressures calculated.

3. No evidence was obtained in support of the curious partial pressure curves which had previously been reported by others.

In conclusion, we wish to thank the Ethyl Gasoline Corporation for the sample of *n*-heptane furnished by them.

REFERENCES

(1) SMYTH AND ENGEL: J. Am. Chem. Soc. **51**, 2660 (1929).
(2) SAMESHIMA: J. Am. Chem. Soc. **40**, 1482 (1918).
(3) FERGUSON: J. Phys. Chem. **36**, 1123 (1932).
BEARE, MCVICAR AND FERGUSON: J. Phys. Chem. **35**, 1068 (1931).
FERGUSON AND FUNNELL: J. Phys. Chem. **33**, 1 (1929).
(4) International Critical Tables, Vol. III, p. 212.
(5) YOUNG: Proc. Roy. Dublin Soc. **12**, 374 (1910).
(6) REGNAULT: Mem. Roy. Acad. Sci. **26**, 339 (1862).

THE SOLUBILITY OF METALLIC LITHIUM IN LIQUID AMMONIA AT LOW TEMPERATURES[1]

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Seely (1) was the first to observe that liquid ammonia dissolves metallic lithium. Following this observation several investigations (2) have been reported relative to the physical properties of lithium solutions.

Although metallic lithium has been regarded as highly soluble in liquid ammonia, Ruff and Geisel (2a) are the only workers to carry out direct quantitative solubility measurements at different temperatures. They filtered the saturated solution through cotton and then analyzed the filtrate for lithium and ammonia. Measurements at 0°, −25°, −50° and −80°C. gave in each case a value of 3.93 gram-molecules of ammonia per gram-atom of lithium for the composition of the saturated solution. The solubility of metallic sodium in ammonia decreases with increasing temperature from −100° to 0°C., while that of metallic potassium increases with increasing temperature over the same temperature range (3). Although the changes in solubility with the temperature are relatively small in these two cases, it is difficult to understand the lack of change in the case of lithium. It appears that the method employed by Ruff and Geisel is not sufficiently accurate to detect small changes in the solubility.

Kraus and Johnson (2f) have measured the vapor pressure of solutions of lithium in liquid ammonia at −39.4°C. from the saturation point to a concentration of 60 gram-molecules of ammonia per gram-atom of lithium. A value of 3.61 NH_3/Li was found for the composition of the saturated solution. The pressure-composition curve offers a convenient means for the determination of the solubility of an alkali metal in this medium. When ammonia is added to the metal, the resulting solution shows a constant vapor pressure, that of the saturated solution, as long as any undissolved metal remains. The change in the vapor pressure in passing from the saturated solution to those less concentrated in metal is very abrupt. When this curve is extrapolated to intersect the horizontal line representing the vapor pressure of the saturated solution, there is obtained a point corresponding to the composition of this solution.

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[1] From a thesis submitted by M. M. Piskur to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science.

In the present investigation the vapor pressure of solutions of lithium in liquid ammonia is determined at 0°, −32.7°, −33.2° and −63.5°C. in order to obtain the composition of the saturated solution as a function of the temperature. The results clearly show the solubility of metallic lithium to increase appreciably with increasing temperature.

APPARATUS AND MATERIALS

The method employed for the vapor pressure measurements was essentially the same as that previously described for lithium solutions (2f). Since most of the experiments were confined to concentrated solutions of the metal, only small amounts of hydrogen were found to be liberated due to a reaction between lithium and ammonia. The hydrogen was removed from the apparatus during the course of a series of measurements in order to obtain true equilibrium pressures.

The measurements were carried out at several different temperatures, 0°, −32.7°, −33.2° and −63.5°C. To maintain the temperature at 0°C., the vapor pressure tube was surrounded by a Pyrex Dewar flask containing finely-chipped ice in equilibrium with water. A thermometer calibrated by the Bureau of Standards was inserted in the bath and the temperature was noted to remain at 0°C. ± 0.05° for a period of several hours. A thin-walled glass tube was placed around the vapor pressure tube in order to keep the lithium separated from the ice-water mixture in case of accident. It was found more difficult to maintain constant temperature in the neighborhood of the normal boiling point of liquid ammonia. The ammonia in the Dewar tube was allowed to boil against a column of mercury of approximately 1 cm. which was exposed to the atmosphere. In addition, the height of the liquid ammonia in the Dewar tube was kept as constant as possible by frequent additions. However, owing to changes in the height of this column and changes in the atmospheric pressure, the variation of the temperature during the course of an experiment was ±0.1°. A temperature of −63.5°C. was obtained with a mixture of liquid nitrogen and chloroform. No difficulty was experienced in keeping this temperature constant to ±0.1°.

The metallic lithium used in the experiments was found to be free of iron and potassium and to contain a small amount of sodium. Liquid ammonia of commerce was siphoned into small steel tanks containing a few grams of metallic sodium as a dehydrating agent. The ammonia was distilled into a second steel container before being used for the experiments.

RESULTS

The results of two series of measurements at 0°C., one series at −32.7°C., one series at −33.2°C., and three series at −63.5°C. are given in table 1. The values obtained at 0°C. are plotted in figure 1, while those at the lower

TABLE 1

Vapor pressure of solutions of lithium in liquid ammonia at different concentrations and temperatures

CONCENTRATION NH₃/Li	PRESSURE	CONCENTRATION NH₃/Li	PRESSURE
Series 1 0 2644 gram of lithium $T = 0°C$			
	mm		*mm*
3 623	34 1	4 323	938 0
3 647	34 9	4 350	876 0
3 667	57 0	4 658	1177 0
3 726	166 5	5 090	1542 0
3 810	252 0	5 590	1857 0
3 890	376 0	6 653	2288 0
3 990	509 0	7 701	2560 0
4 111	660 0		
Series 2 0 1187 gram of lithium $T = 0°C$			
3 542	34 0	3 750	207 0
3 580	34 0	3 875	381 0
3 610	41 0	4 092	642 0
3 639	67 0	4 467	1048 0
3 680	115 5		
Series 3 0 1968 gram of lithium $T = -32\ 7°C$			
3 739	3 3	4 363	260 5
3 741	3 4	4 521	310 0
3 764	8 0	4 715	360 8
3 802	25 0	4 938	409 5
3 858	56 0	5 175	449 2
3 921	94 5	5 446	490 4
3 987	119 0	5 723	525 7
4 056	146 5	5 950	550 0
4 142	178 8	6 288	580 0
4 242	218 4	6 495	597 5
Series 4 0 1818 gram of lithium $T = -33\ 2°C$			
3 747	3 4	4 127	172 3
3 750	3 4	4 233	213 0
3 753	3 7	4 373	259 0
3 789	10 9	4 542	309 4
3 805	22 3	4 712	362 0
3 858	51 5	5 002	412 0
3 930	87 2	5 296	458 0
3 985	109 0	5 603	501 0
4 046	136 5	5 830	526 5

TABLE 1—*Concluded*

CONCENTRATION NH_3/Li	PRESSURE	CONCENTRATION NH_3/Li	PRESSURE
Series 5. 0.0762 gram of lithium $T = -63.5°C.$			
	mm.		*mm.*
4.039	25.8	5.714	94.0
4.229	43.7	6.348	103.6
4.602	62.8	7.279	108.6
5.091	80.8		
Series 6. 0.0922 gram of lithium. $T = -63.5°C.$			
3.824	1.8	4.034	21.9
3.854	4.0	4.288	42.5
3.898	8.7		
Series 7. 0.1015 gram of lithium. $T = -63.5°C.$			
3.811	1.2	3.980	18.3
3.820	2.5	4.061	26.0
3.852	5.5	4.174	35.9
3.924	10.0	4.330	48.5

temperatures are shown in figure 2. Many of the values are not plotted, especially in the concentrated regions, owing to overlapping of points. The measurements at −32.7°C. and −33.2°C. are plotted together. Since most of these values appear at high lithium concentrations, where the change in the vapor pressure with the temperature is very small, the two series of measurements fall closely together. The concentrations are expressed in gram-molecules af ammonia per gram-atom of lithium, while the pressures are given in millimeters of mercury.

The composition of the saturated solution was determined at each temperature by an extrapolation of the curves shown in figures 1 and 2. Additional experiments were carried out with an excess of metallic lithium present in order to establish the vapor pressure of the saturated solution at these temperatures. The data are shown in table 2.

DISCUSSION OF RESULTS

Figures 1 and 2 show the vapor pressure of lithium solutions at different temperatures and over a relatively small range of concentration. These curves are identical in form with that obtained previously for lithium solutions at −39.4°C. (2f). There is no indication of a combination between lithium and ammonia; nor is there any evidence for the existence of a two-phase liquid system at the lowest temperature studied. Ruff and Zedner

(2b) point out the appearance of a two-phase liquid system for lithium solutions below −35°C. The above results indicate the non-existence of such a system within the range of concentrations employed, namely, between 3.81 and 7.28 gram-molecules of ammonia per gram-atom of lithium, since the vapor pressure curves do not show any irregularities.

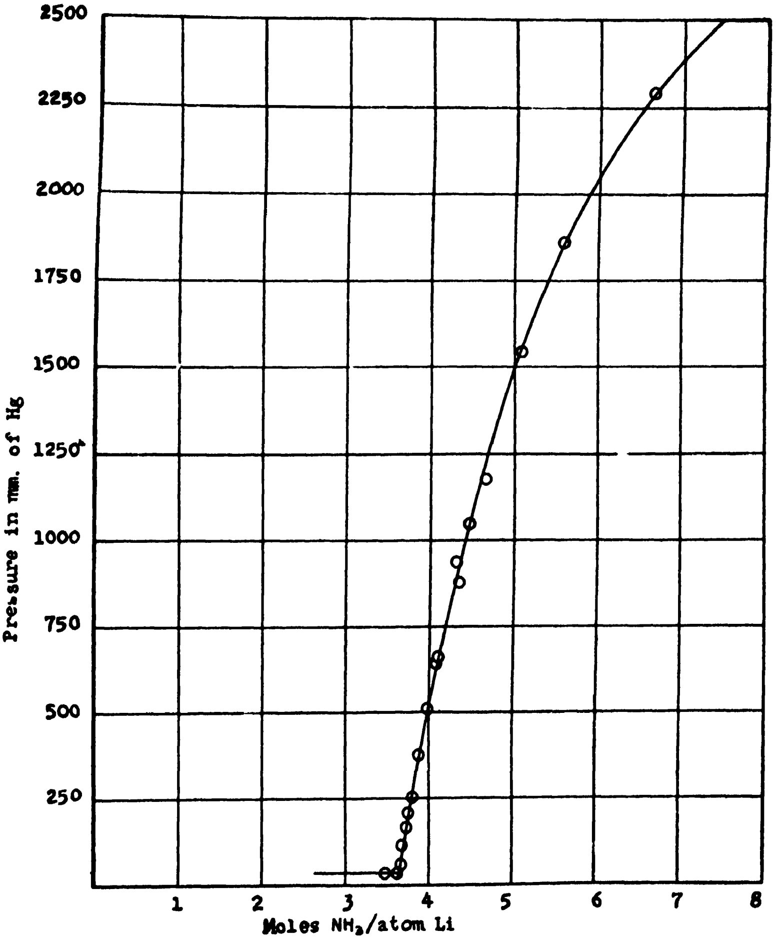

Fig. 1. The Vapor Pressure of Lithium Solutions at 0°C.

It is quite probable that a new liquid phase does appear at lower lithium concentrations as is the case with sodium solutions (4).

It is also evident that the solubility of metallic lithium in liquid ammonia increases appreciably with increasing temperature. This increase amounts to approximately 6 per cent from −63.5°C. to 0°C. The vapor pressure

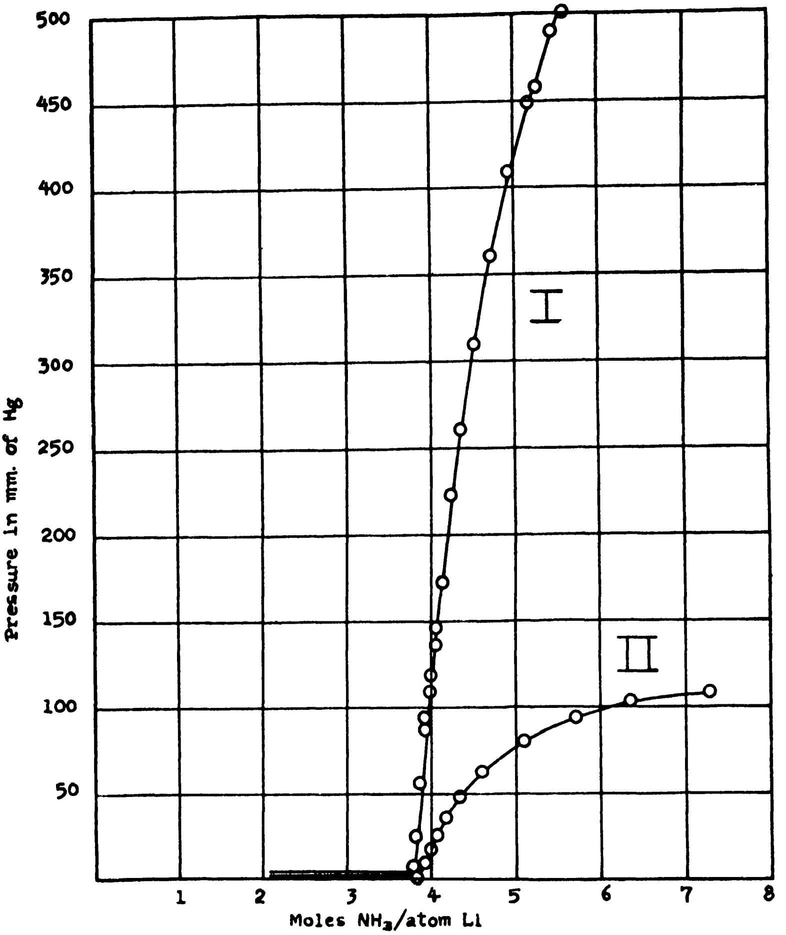

FIG. 2 THE VAPOR PRESSURE OF LITHIUM SOLUTIONS AT −33°C. (I), AND AT −63 5°C (II)

TABLE 2

Vapor pressure and composition of saturated solutions

TEMPERATURE	VAPOR PRESSURE	MOLES NH_3/Li	GRAMS Li PER 100 GRAMS NH_3
°C	*mm*		
0°	34 0	3 60	11 319
−32 7°	3 4	3 74	10 895
−33 2°	3 4	3 75	10 866
−63 5°	1 1	3 81	10 698

of the saturated solution increases markedly throughout this same temperature range. The value obtained at 0°C., 34 mm., agrees well with that found by Kraus (2c), namely 33 mm. Kraus and Johnson (2f) found the composition of the saturated solution at −39.4°C. to be 3.61 gram-molecules of ammonia per gram-atom of lithium; our value at a slightly higher temperature is 3.74. This difference of approximately 3 per cent may be ascribed to the presence of foreign elements, particularly iron, sodium, and potassium, in the various samples of metallic lithium used in the two investigations. In the present work, samples of lithium were taken from the same source; each sample failed to show the presence of iron and potassium but appreciable quantities of sodium were found. However, the maximum amount of sodium that could be present with the lithium, according to the results of the analytical determinations, would not seriously change the composition of the saturated solutions in our experiments, certainly not more than 1 per cent. Experiments are now being undertaken to make direct solubility measurements of the alkali metals in liquid ammonia which promise to yield results of a higher accuracy than is allowed by the indirect vapor pressure method.

SUMMARY

The vapor pressure of solutions of lithium in liquid ammonia has been determined at high lithium concentrations and at several temperatures. An extrapolation method is used to obtain the composition of the saturated solution at each temperature. The results show the solubility of metallic lithium to increase appreciably from −63.5° to 0°C.

REFERENCES

(1) Seely: Chem. News **23**, 169 (1871).
(2) (a) Ruff and Geisel: Ber. **39**, 828 (1906).
  (b) Ruff and Zedner: Ber. **41**, 1948 (1908).
  (c) Kraus: J. Am. Chem. Soc. **30**, 653 (1908).
  (d) Kraus: J. Am. Chem. Soc. **43**, 749 (1921).
  (e) Benoit: Bull. soc. chim. **33**, 908 (1923).
  (f) Kraus and Johnson: J. Am. Chem. Soc. **47**, 725 (1925).
(3) Johnson and Meyer: Chem. Rev. **8**, 273 (1931) for data and references.
(4) Kraus and Lucasse: J. Am. Chem. Soc. **44**, 1949 (1922).

THE SYSTEM AMMONIA-WATER AT TEMPERATURES UP TO 150°C. AND AT PRESSURES UP TO TWENTY ATMOSPHERES

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INTRODUCTION

The total vapor pressures of ammonia-water solutions at temperatures between 0°C. and 120°C. and at pressures up to 9 atmospheres have been measured by Mollier (1) who, however, determined no vapor compositions. Smits and Postma (2) examined the system in the region of the eutectic points and three-phase lines. They determined the pressures, temperatures, and compositions of certain solutions, including those existing in equilibrium with the various solid phases. Perman (3) has determined both total vapor pressures and vapor compositions between 0°C. and 60°C. at pressures below atmospheric.

Perman's method consists of passing a known volume of air through the ammonia solution, and determining the weights of ammonia and water the air takes up. The partial vapor pressures of ammonia and of water can then be calculated from these weights, and the total pressure of the air-ammonia-water vapor phase.

The work now reported was carried out in order to extend the knowledge of this system up to 150°C. and 20 atmospheres pressure. A dynamic method was used to determine vapor compositions between 60°C. and 100°C. and for pressures up to 1.5 atmospheres. The method was inconvenient for higher pressures.

The total vapor pressures in the system up to 9 atmospheres were already known (4).

For the higher range of temperatures and pressures it was found necessary to use a static method. Both total vapor pressures and vapor compositions were measured.

EXPERIMENTAL

1. From 60°C. to 100°C.; pressures up to 1.5 atmospheres

At temperatures as high as 60°C., Perman had difficulty in getting the air he passed through his saturators containing the ammonia solutions to take up its proper amount of ammonia and water. As saturators he used vessels of the wash-bottle type, and his difficulties were most probably due to the inefficiency of these when called upon to saturate air with the large quantities of ammonia and water provided by the high partial pressures at 60°C.

A very efficient saturator designed by Bichowsky and Storch (5) has been adapted for vapor pressure work by Pierce and Snow (6). Its design is shown in figure 1a.

The solution is held in the tube A. Air enters at B and breaks into bubbles at the jet C. These bubbles travel up the inclined tube D, becoming saturated with vapor from the solution. At the surface of the solution they break and the vapor travels back to the outlet at E. Behind and below the jet C, a vent F is blown in the tube D. Here solution is drawn in and carried up the tube D between the bubbles. This ensures thorough mixing of the solution. The neck G, provided for filling purposes, is closed by a rubber stopper which can be wired on. A sample of the solution can be withdrawn by way of the capillary tube H.

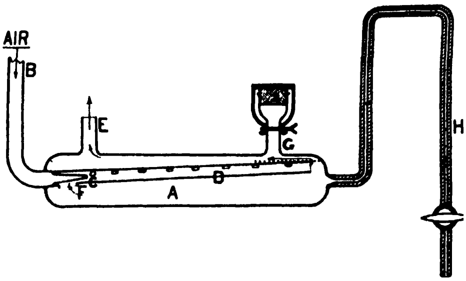

Fig. 1a

Four vessels of this pattern, each 10 in. x 1½ in., made of Pyrex glass, were joined together in series in the way shown in figure 1b. It was not considered necessary to provide the two inner vessels with sampling tubes. The inlet and outlet tubes A and B were vertical. The whole apparatus was mounted in a frame which could be held in a thermostat capable of regulation to ±0.01°C. The water level in the thermostat was maintained well above the stopper C. To prevent condensation from the gas on the walls of the tube B a heating coil D formed on a brass tube surrounding B was used. The tube was heated to 120–140°C.

The air supply was kept at a suitable pressure, indicated by the manometer E, by adjusting the screw clip F on a tube opening to the atmosphere. The clip G regulated the supply to the apparatus. Rubber pressure tubing was used, wired on at all connections.

The method of using the apparatus depended upon whether the solution in the saturators had a total vapor pressure below or above approximately 650 mm. at the working temperature. With the former type of solution it is possible to pass through a sufficient amount of air without taking the pressure above atmospheric; this method will be described first.

The saturators were filled to the correct level (the top of the inclined tubes) with an ammonia solution of known composition. After wiring on the stoppers the apparatus was placed in the thermostat and the heating coil was fitted over the outlet tube B. The pressure tubing from the air supply already described was wired on to the tube A with the clip G closed. A length of about 6 inches of Pyrex tubing (3-mm. bore) was sealed to the top of the tube B, and bent over at right angles, as shown at J in figure 2. The current to the heating coil and thermostat was then switched on, and the latter was brought to the working temperature and there regulated.

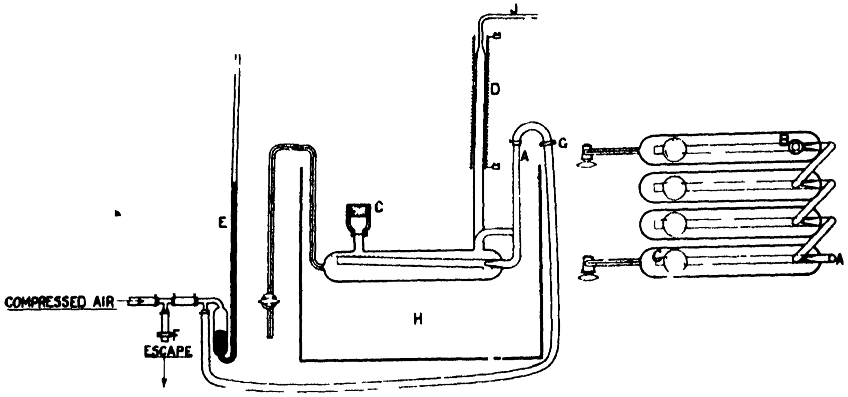

FIG 1b

The absorption train consisted of two U-tubes, the first containing glass beads covered with 25 per cent sulfuric acid, the second, glass beads with concentrated sulfuric acid. A third tube filled with glass wool–phosphorus pentoxide absorbent was eventually discarded, for its weight never increased by more than one-fifth of a milligram during a run.

The absorption train, after preparation and weighing, was fitted to the tube J with pressure tubing.

The clip G was carefully adjusted to allow a slow, steady stream of bubbles to form and to pass through the apparatus and absorption system. During the run the tube J was gently warmed with a Bunsen flame to prevent condensation before the vapor reached the U-tubes. After a run, the clip G was closed and the absorption train was disconnected and weighed. The contents of the U-tubes were washed out, and the ammonia present was determined by distillation. The increase in weight of the U-tubes was normally between 0.5 and 1.0 gram.

Finally a sample of the solution in the saturators was removed for analysis. A change in composition of one part per hundred of the NH_3 percentage was sometimes observed in the first saturator, where the air was admitted; in the last saturator the composition of the solution was always within 0.2 part per hundred of the original NH_3 percentage. The composition of the solution in the last saturator was taken as that of the solution in equilibrium with the vapor collected.

For solutions of the second type, those with total pressures between 650 mm. and 1100 mm. at the working temperature, it was necessary to devise some way of keeping the pressure in the saturators and absorption train at least 100 mm. above the total vapor pressure of the solution, in order to provide sufficient air to take up the ammonia and water. The apparatus shown in figure 2 was used. The U-tube A was made of Pyrex tubing (3-mm. bore) widening to 11–mm. bore tubing at the U. To the base of the U, a third tube, B, was sealed and bent upwards. This was connected to the 50-cc. pipette bulb C, fitted to pressure tubing provided with the screw clip D. The apparatus was held in an oven, E, fitted with mica windows. The oven was heated to keep the vapor passing through the U above its dew point. The side arm F was connected to the absorption system, the far end of which was connected to the tube H, dipping into a column of mercury, and to the tap K. The U-tube A was filled with mercury to the level L.

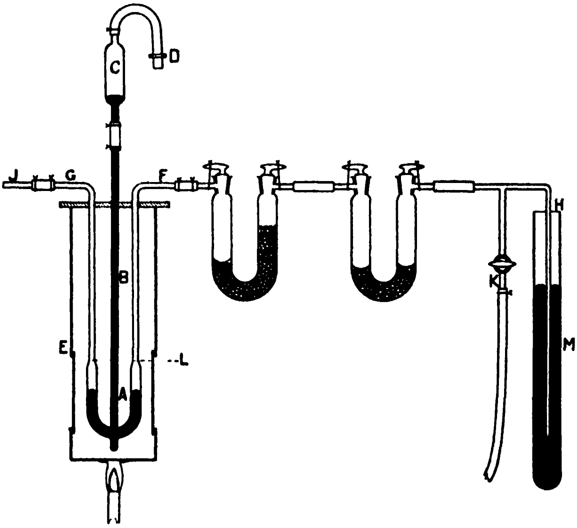

Fig. 2

In preparation for a run, the apparatus was assembled in the way shown in figure 3. The taps of the absorption tubes and all rubber connections were wired on, and the warming up of the oven E was begun. The saturators were prepared as before, but when the temperature of the thermostat had risen to a point where the total vapor pressure of the complex in the saturators had reached approximately 650 mm., the tube J (from the saturators) was connected to the limb G of the U-tube with pressure tubing which was wired on. Subsequently, as the temperature of the thermostat rose towards the working temperature, the pressure of air, ammonia vapor, and water vapor in the saturators rose steadily. This increase of pressure was balanced by applying a pressure of air through the tap K at intervals, and watching the level of mercury in the limbs of A. After the thermostat had reached the working temperature and had been regulated, the mercury in A was drawn up into the bulb C, until there was a free passage for the vapor from one limb of A to the other, and the clip D was closed. Air was then admitted to the saturators and the run proceeded. The air finally escaped through H, bubbling up the tube M. Again, it was necessary to keep the upper tubes J, G, and F gently warmed. The run was brought to an end by shutting off the air supply to the saturators and releasing the mercury in the bulb C, which closed the passage between G and F. The length of the limb F was usually sufficient to take

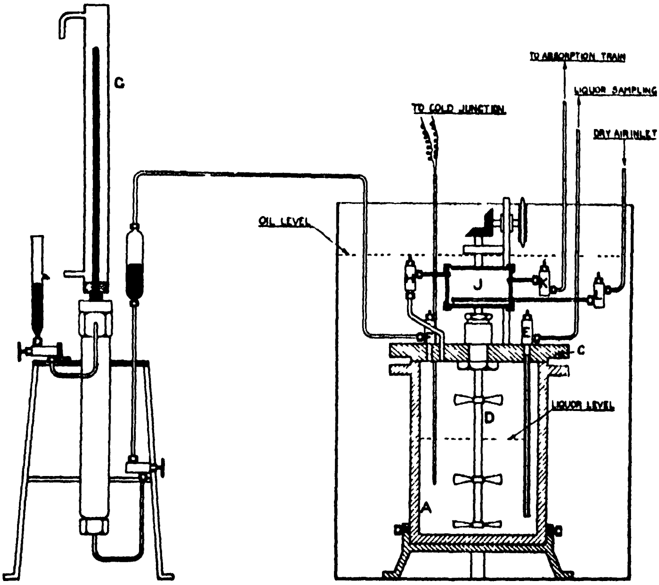

FIG. 3

the column of mercury which rose (owing to the pressure difference) when the absorption train was disconnected for weighing. At the highest pressures it was occasionally necessary to allow the thermostat to cool for some time before detaching the absorption tubes.

Results

The results which were obtained are given in table 1. The total vapor pressures were obtained by interpolation of the values given in the International Critical Tables, Vol. VIII, p. 362. The figures for the ammonia content of the vapors are probably accurate to 1.5 units for vapors of composition 30–70 per cent of ammonia. Beyond these limits these determinations are believed to be more accurate.

2. From 100°C. to 150°C.; pressures up to 20 atmospheres

The apparatus which was used had been designed for the determination of the equilibrium relations of pressure, temperature, and compositions of solutions and vapors in uncondensed systems, at temperatures above 100°C. and pressures below 20 atmospheres. A 4-liter bomb is used to hold the complex, the vapor volume being about two liters. There are arrangements for stirring, for measuring the temperature and pressure, and for withdrawing for analysis samples of solution and vapor.

The apparatus is shown diagrammatically in figure 3. The bomb A, of stainless iron, is closed by bolting down the cover, C, over a copper washer. In the centre of this cover is a pressure gland through which the stirrer D passes. The gland is packed with S. E. A. rings, and the stirrer rotates at 60 r.p.m. and has paddles in the liquor and vapor. Screwed on to the cover are two valves, E and F. Valve E has attached a tube which dips into the bomb to within an inch and a half of the bottom. The opening of F is flush with the lower side of the cover, and this valve connects the apparatus to the closed hydrogen manometer G, which is capable of measuring pressures up to 20 atmospheres. A connection from the cover of A to the valve H leads to a smaller bomb J (300 cc.) which is held on to the cover by a bracket. This smaller bomb is fitted with two valves K and L, K for withdrawing the vapor sample to an adsorption train, and L for the inlet of dry air to the farther end of J for sweeping out the contents. A copper–constantan thermocouple in a sheath is also fitted through the cover of A, a lens-ring joint being used. To avoid the use of compensating leads, the thermocouple wires run directly to a cold junction and potentiometer. The apparatus is held in position by fixing the bomb A in a tripod in the base of an oil thermostat, the oil level being above the top of the smaller bomb J.

The thermocouple was calibrated at 10°C. intervals up to 200°C., and can be read accurately to within 0.1°C. The closed manometer is filled with pure dry hydrogen, and the column of gas is water-jacketed. The volume of the capillary had been determined for each 2 cm. of its 70 cm. length. In order to calculate the pressure of the hydrogen from the height

TABLE 1

PRESSURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	T = 60 0°C	
atmospheres	*per cent*	*per cent*
0 240	0 96	17 2
0 286	1 97	28 8
0 355	3 40	40 8 39 1
0 366	3 66	43 1
0 416	4 69	55 2 55 3
0 430	4 94	55 6
0 487	6 04	60 2
0 584	7 90	69 6
0 630	8 66	72 3
0 842	11 99	79 3 79 2
1 104	15 38	84 2
1 451	18 91	90 0
	T = 80 0°C	
0 546	0 96	14 3
0.634	1 97	28 2
0 761	3 40	38 1
0 786	3 66	41 1
1 030	6 04	53 1
1 224	7 90	63 1
1 705	11 9	73 6 73 4
	T = 90 0°C	
0 742	0 50	6 90
0 797	0 96	13 12
0 855	1 47	19 2
0 916	1 97	23 4
0 957	2 26	29 4
1 124	3 7	38.7
1 364	5 54	49 8
	T = 100.0°C.	
1 064	0 50	6 14
1 205	1 47	18 0
1 433	2 98	31 6

of mercury in the capillary, it was necessary to know the quantity of hydrogen enclosed in the capillary. This was found by calibration against an open mercury column manometer at 2 atmospheres pressure. In addition, the higher pressure readings of the manometer (5 to 20 atmospheres) were checked against a calibrated Bourdon gauge. A cathetometer was used to read the position of the mercury in the capillary and to measure the difference in level of the mercury in the capillary and in the reservoir. The pressure due to this head of mercury must be added to the calculated hydrogen pressure to give the pressure applied to the manometer. By closing a valve which lies between the reservoir and the body of the manometer, the gas space above the mercury in the reservoir could be evacuated without removing hydrogen from the capillary.

To put a complex in the bomb the apparatus was evacuated while standing at room temperature and the valve H closed. Two liters of complex was then drawn into the bomb A through the liquor sampling tube, care being taken not to introduce air with the complex. The thermostat was heated to the working temperature and regulated, and the contents of the bomb were stirred at this steady temperature overnight. This was found to be a sufficient length of time to establish equilibrium. The manometer and thermocouple readings were taken. After evacuating the vapor sampling bomb J, the valve H was quickly opened and closed, isolating in J a sample of the vapor. The sample was drawn out by way of the valve K, through a sulfuric acid absorption train for analysis. When the pressure had been reduced to that of the service vacuum, air drawn through concentrated sulfuric acid was admitted through the valve L, and was swept through the bomb and train to remove the last traces of water and ammonia from J. Samples of solution were taken by opening the valve E and absorbing a few grams of the complex in a known weight of sulfuric acid in a system of traps which excluded the possibility of any loss of sample or acid.

Usually a given complex was examined at a whole series of temperatures between 100°C. and 150°C. New complexes were obtained either by emptying and re-filling the bomb, or by boiling off vapor from the previous complex. After some of the results had been obtained, it was found that the temperature of the complex in the bomb measured by the thermocouple, was always 3°C. below that of the outside bath, owing to heat losses through the connections from the bomb. This temperature difference was confirmed by experiments on the vapor pressure of water measured at a number of temperatures in this apparatus. In order to make use of these first results the work was continued at 97°C., 107°C., 117°C., 127°C., 137°C. and 147°C.

Results

The experimental results are given in table 2. The error in the compositions in most of these, is about one part per hundred of the ammonia

TABLE 2

Isotherms of the system, ammonia–water

PRESSURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	T = 97°C	
atmospheres	*per cent*	*per cent*
0.899	0	0
2.4	9.3	63.3
3.8	16.0	78.3 76.0
6.76	25.5	89.76 89.58
7.04	25.9	89.6
	T = 107°C.	
1.277	0	0
3.27	10.0	61.0 60.0
5.12	16.0	75.3
8.55	25.0	86.4
	T = 117°C.	
1.780	0	0
3.35	6.5	—
4.35	9.5	61.5
5.8	14.7	73.2
10.63	—	83.1
	T = 127°C.	
2.435	0	0
4.37	6.43	45.3 43.7
5.62	9.5	59.0
7.31	—	68.5
12.44	—	79.1
13.6	25.0	82.5 82.8
	T = 137°C.	
3.274	0	0
5.7	6.5	42.0
9.06	—	66.2 65.9
14.90	—	78.5
—	25.0	80.2
	T = 147°C.	
4.332	0	0
7.3	6.5	40.2 40.6
9.3	9.5	50.2
11.84	13.6	62.4 62.0
16.3	19.5	75.0

percentage. In some cases, particularly at the highest temperatures, the error in the vapor compositions is two parts per hundred. The error in the total vapor pressure determinations is less than two per cent.

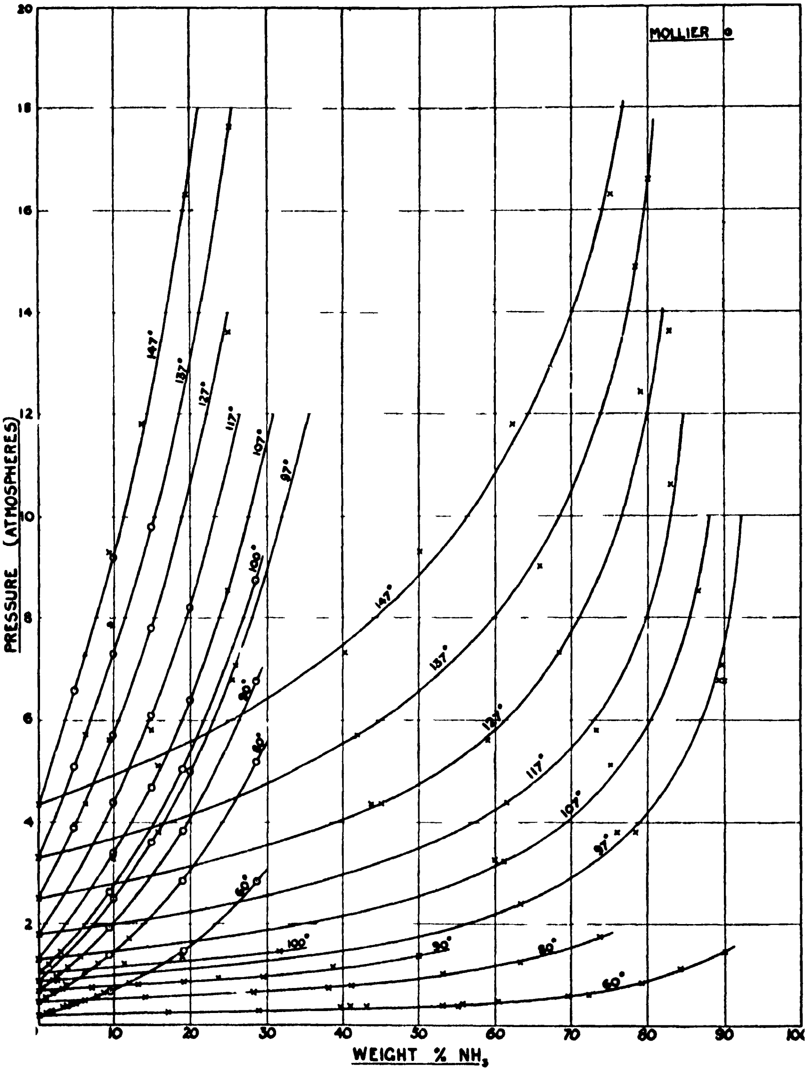

FIG 4

THE ISOTHERMS AND ISOBARS IN THE SYSTEM

The experimental results are plotted as isotherms in figure 4. Data from tables of total vapor pressures given by Mollier (1) obtained by

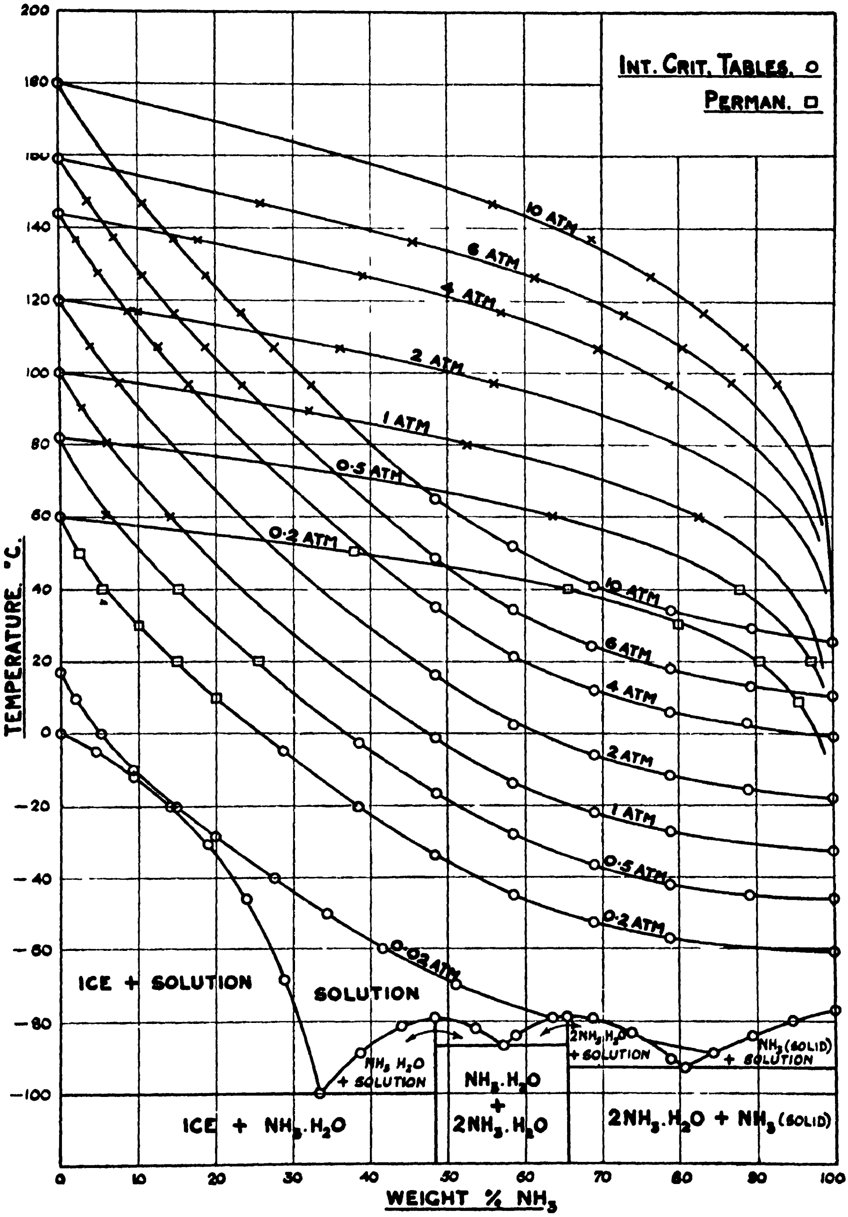
INT. CRIT. TABLES. ○
PERMAN. □
10 ATM
6 ATM
4 ATM
2 ATM
1 ATM
0·5 ATM
0·2 ATM
10 ATM
6 ATM
4 ATM
2 ATM
1 ATM
0·5 ATM
0·2 ATM
0·02 ATM
ICE + SOLUTION
SOLUTION
NH3.H2O + SOLUTION
2NH3.H2O + SOLUTION
NH3 (SOLID) + SOLUTION
ICE + NH3.H2O
NH3.H2O + 2NH3.H2O
2NH3.H2O + NH3 (SOLID)
TEMPERATURE. °C.
200
180
160
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
0
10
20
30
40
50
60
70
80
90
100
WEIGHT % NH3

FIG. 5

TABLE 3

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 10 atmospheres	
degrees C	*per cent*	*per cent*
180 5	0	0
170	3 4	20 5
160	6 6	36 3
150	10 1	51 5
140	14 0	64 8
130	18 0	74 2
120	22 0	81 1
110	26 3	87 0
100	30 8	91 7
90	35 6	95 1
80	40 6	97 4
70	46 0	98 8
60	52 2	
50	60 0	
40	70 2	
30	87 0	
25 3	100	100
	Pressure = 8 atmospheres	
171	0	0
170	0 3	2 3
160	3 1	20 7
150	6 4	38 9
140	10 2	55 5
130	14 1	68 0
120	18 3	77 3
110	22 4	84 0
100	26 7	89 5
90	31 4	93 3
80	36 4	96 2
70	41 9	98 2
60	47 5	
50	54 1	
40	62 0	
30	73 5	
20	94 6	
18 5	100	100
	Pressure = 6 atmospheres	
159 3	0	0
150	2 6	19 5
140	5 9	40 0
130	9 6	57 1
120	13 5	69 9

TABLE 3—*Continued*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 6 atmospheres—*Concluded*	
degrees C	*per cent*	*per cent*
110	17 6	78 4
100	22 0	84 8
90	26 6	90 0
80	31 4	94 2
70	36 6	97 0
60	41 9	
50	47 5	
40	54 0	
30	62 0	
20	74 6	
9 7	100	100
	Pressure = 4 atmospheres	
144 1	0	0
140	1 0	9 8
130	4 2	33 0
120	7 7	52 2
110	11 5	66 3
100	15 5	76 0
90	19 8	83 6
80	24 4	90 0
70	29 2	94 8
60	34 2	97 3
50	39 7	
40	45 5	
30	52 2	
20	60 2	
10	71 5	
0	94 7	
−1 5	100	100
	Pressure = 2 atmospheres	
120 6	0	0
120	0 15	1 5
110	2 9	29 0
100	6 2	50 6
90	10 0	67 5
80	14 0	80 3
70	18 5	89 2
60	23 4	94 8
50	28 5	97 5
40	33 7	98 4
30	39 3	

TABLE 3—*Continued*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 2 atmospheres—*Concluded*	
degrees C	*per cent*	*per cent*
20	45.6	
10	52.6	
0	61.4	
−10	75.0	
−18.5	100	100
	Pressure = 1 atmosphere	
100	0	0
90	2.9	31.8
80	6.1	52.6
70	10.0	70.0
60	14.4	82.5
50	19.0	90.2
40	24.0	94.5
30	29.1	97.0
20	34.6	98.5
10	40.6	99.2
0	47.3	
−10	55.3	
−20	65.4	
−30	86.0	
−33.2	100	100
	Pressure = 0.5 atmosphere	
81.7	0	0
80.0	0.3	4.5
60	6.2	63.6
40	15.0	87.5
20	26.0	97.5
0	37.2	
−10	43.1	
−20	51.2	
−30	60.0	
−40	75.3	
−46.3	100	100
	Pressure = 0.2 atmosphere	
60.4	0	0
50	2.7	38.0
40	5.5	65.5
30	10.0	80.0
20	15.0	90.5

TABLE 3—*Concluded*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
Pressure = 0.2 atmosphere—*Concluded*		
degrees C	*per cent*	*per cent*
10	20.0	95.5
0	25.3	98.0
−10	31.8	99.0
−61.0	100	100
Pressure = 0.02 atmosphere		
17.7	0	—
10	1.7	—
0	5.0	—
−10	9.5	—
−20	15.0	—
−30	21.0	—
−40	27.5	—
−50	34.3	—
−60	41.5	—
−70	51.0	—
−79.8	62.8	—
−82.9	75.5	—

extrapolation of results determined up to 120°C. and 9 atmospheres, are also plotted on this graph and the agreement is good.

Points from these isotherms, and from those of Perman, together with total vapor pressure values given in International Critical Tables (4) have been used to construct the isobars from 0.02 to 10 atmospheres in figure 5.

The vapor branch of the 0.02 atmosphere isobar is unknown. A projection of the liquid and vapor and solid lines, determined by Smits and Postma, on the $t - x$ base is shown on this figure and defines the lower temperature limits of existence of the solution phase.

The course of the vapor branches of the isobars from 2 atmospheres to 10 atmospheres is somewhat uncertain in the temperature range 70° to 90°C., where no vapor compositions have been determined and where there is a rapid change of curvature, but from analogy with the isobars of lower pressures, it is believed that the curves given in figure 5 are substantially accurate to within 1 per cent of the ammonia concentration. There are no points above 147°C. except those for pure water, but there is little doubt of the positions of the isobars since the curvature is so small in this region.

Tables 3 and 4 have been constructed from figure 5. The values above 10 atmospheres in table 4 were obtained by interpolation of the straight

TABLE 4

AMMONIA IN LIQUOR	PRESSURE	AMMONIA IN VAPOR
	T = 60°C.	
per cent	*atmospheres*	*per cent*
0	0 197	0
5	0 439	56 4
10	0 717	75 8
15	1 084	84 1
20	1 559	91 3
	T = 80°C.	
0	0 467	0
5	0 90	47 8
10	1 48	69 9
15	2 19	81 2
20	3 05	87 0
25	4 14	90 8
30	5 55	93 3
	T = 90°C.	
0	0 692	0
5	1 30	48 5
10	2 00	67 5
15	2 91	77 1
20	4 12	84 5
25	5 55	89 1
30	7 12	92 4
	T = 100°C.	
0	1	0
5	1 82	45 6
10	2 75	64 5
15	3 88	75 3
20	5 31	82 8
25	7 18	87 9
30	9 48	91 3
	T = 110°C.	
0	1 414	0
5	2 41	41 8
10	3 58	61 5
15	5 03	73 7
20	6 91	81 4
25	9 20	86 2
30	11 98	89 0

TABLE 4—*Concluded*

AMMONIA IN LIQUOR	PRESSURE	AMMONIA IN VAPOR
	T = 120°C.	
per cent	*atmospheres*	*per cent*
0	1 96	0
5	3 22	39 3
10	4 70	60 0
15	6 55	72 7
20	8 83	79 2
25	11 72	83 2
30	15 46	—
	T = 130°C.	
0	2 67	0
5	4 27	37 7
10	6 15	58 2
15	8 42	69 6
20	11 33	76 8
25	15 04	82 0
30	19 8	—
	T = 140°C	
0	3 57	0
5	5 55	34 7
10	7 83	53 8
15	10 70	67 2
20	14 37	75 7
25	19 20	—
30	—	—
	T = 150°C.	
0	4 70	0
5	7 14	31 3
10	10 02	31 5
15	13 58	66 4
20	18 6	75 5
25	—	—
30	—	—

lines obtained when log P is plotted against the reciprocal of the absolute temperature.

SUMMARY

1. The compositions of the vapors in equilibrium with ammonia–water solutions have been determined at 60°C., 80°C., 90°C., and 100°C. for solutions with total vapor pressures up to 1.5 atmospheres.

2. The total vapor pressures and compositions of vapors in equilibrium with ammonia-water solutions have been determined within the limits 100–150°C. and 1 to 20 atmospheres.

3. The isotherms in the system have been constructed for temperature intervals between 60°C. and 150°C.

4. From the results of the work reported and those of Perman, Mollier, and Smits and Postma (3, 1, 2), the isobars for 10, 8, 6, 4, 2, 1, 0.5, 0.2 and 0.02 atmospheres have been obtained.

The authors wish to express their thanks to the Directors of Imperial Chemical Industries Ltd., for their permission to publish this work, which was carried out in the Research Laboratory of their subsidiary company, I. C. I. (Alkali) Ltd.

REFERENCES

(1) Mollier: Z. Ver. deut. Ing. **52**, 2, 1315 (1908).
(2) Smits and Postma: Proc. Acad. Sci. Amsterdam **17** (1), 182 (1914).
(3) Perman: J. Chem. Soc. **83**, 1168 (1903).
(4) International Critical Tables, Vol. III, pp. 362, 234.
(5) Bichowsky and Storch: J. Am Chem. Soc. **37**, 2696 (1915).
(6) Pierce and Snow: J. Phys. Chem **31**, 231 (1927)

THE ELECTRICAL CONDUCTIVITY OF COMMERCIAL DIELECTRICS AND ITS VARIATION WITH TEMPERATURE[1]

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THEORY

It has long been known that the electrical resistance of a material to which the term "dielectric" is applied is a function of the temperature, decreasing as the temperature increases. Thus, in 1889 Curie (1) found that the specific volume resistance of quartz in the direction of the optical axis fell from 1.2×10^{14} ohm-cm. at 20°C. to 5.6×10^{7} ohm-cm. at 300°C., and Campbell (2) in 1913 reported that this quantity decreased from more than 2×10^{14} ohm-cm. at 15°C. to 2×10^{7} ohm-cm. at 800°C. for the same substance after fusion.

In 1906, Koenigsberger and Reichenheim (3), assuming that the conduction through dielectrics (oxides, sulfides, metals, and metalloids) is largely electronic in nature, developed an equation to express the change of resistance with temperature as follows:

$$R_t = R_0 (1 + at + bt^2)\, e^{-qt/273(273 + t)} \tag{1}$$

where R_t is the specific volume resistance at temperature t (in degrees Centigrade), R_0 is the specific volume resistance at zero degrees Centigrade, and q is a constant characteristic of the material. The quantities a and b, also constants, usually become negligible for dielectrics, so that the equation reduces to

$$R_t = R_0\, e^{-qt/273(273 + t)} \tag{2}$$

This equation may also be expressed in logarithmic form

$$\log R = A + B/T \tag{3}$$

where R is the specific volume resistance, T is the absolute temperature, and A and B are constants. This form of equation, which may also be derived, as will be shown later, by assuming that the conduction process is an ionic one, was tested by Rasch and Hinrichsen (4) in 1908, by Pirani and Siemens (5) in 1909, by Dietrich (6) in 1910, and by Curtis (7) in 1914. In these investigations the behavior of both crystalline and amorphous dielectrics was studied.

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[1] This article is adapted from the thesis of J. D. Clark, submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the University of Wisconsin.

In 1926 Saegusa (8) measured the resistance of quartz, calcite, ambroid, paper, and paraffin at temperatures ranging from 10°C. to 360°C., and developed another formula to express his results. The conductivity was assumed to be electronic in nature. The electrons are thermionic in origin according to this investigator. The formula developed was

$$\bar{\mu} = ATe^{-q/kT}\left(1 - BT^2e^{-q/kT} - CTe^{-q/kT}\right) \tag{4}$$

where $\bar{\mu}$ is the specific volume conductivity, T is the absolute temperature, k is the Boltzmann constant, q is the work of liberation of one electron, and A, B, and C are constants which are made up as follows:

$$A = l\bar{v}\epsilon^2 \frac{A'}{4k}, \quad B = 2\rho^2 A', \quad C = 2\rho\epsilon^2 \frac{A'}{k}$$

In these expressions l is the mean free path of an electron, $\bar{v}$ is the mean velocity of an electron, ρ is the effective radius of an atom of the dielectric, ϵ is the electronic charge, and A' is a constant specific for each material.

Joffe (9) has developed the following equation to express the conductivity of a pure crystal as a function of the temperature:

$$\log \bar{\mu} = -a/T + b \tag{5}$$

Here a and b are constants, $\bar{\mu}$ is the specific volume conductivity, and T is the absolute temperature. This equation, having the form of equation 3, was developed using the assumption that the conductivity is the result of an ionic process. It will be shown later that an equation of the same sort may be developed and applied with some success when the dielectric is not a pure crystal.

APPARATUS AND PROCEDURE

The usual method of measuring very high resistances involves the use of a ballistic galvanometer. The use of this instrument is disadvantageous from more than one point of view. The galvanometer must be calibrated and must be kept in calibration. A slight variation in the characteristics of any part of the apparatus, or a slight variation in the technique of operation, serves to introduce errors into any result. These disadvantages are inherent not only in a ballistic galvanometer, but also in a calibrated electrometer when it is substituted for the former, and in any type of instrument which depends upon a scale reading for the results. When it is possible to use it a null method is more desirable.

The Wheatstone bridge is the commonest of all zero reading instruments for this type of work. It is not usually adapted to the measurements of very high resistances, since the ratio of the two resistance arms of the bridge becomes very high near the limit of the range of operation, with a resultant loss in accuracy. However, it has so many advantages in ease of operation, in reliability and in stability with respect to slight variations in the indicating instrument that it was decided to modify it to an extent that would make it suitable for the measurement of very high resistances. In this modification a Compton electrometer was substituted for the usual galvanometer to increase the sensitivity of the arrangement. But the most important change from the usual bridge was the elimination of two variable resistances with the insertion of voltages in their places. A diagram of the apparatus as used is shown in figure 1. Thus by increasing the voltage on what would normally be the high resistance side of the

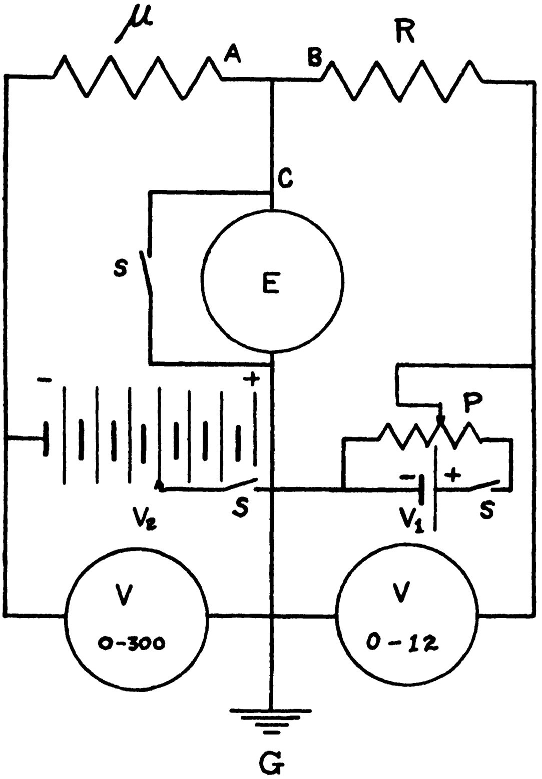

FIG. 1. DIAGRAM OF MEASURING CIRCUIT

μ, unknown resistance; R, standard resistance; P, potentiometer; V, voltmeter; E, electrometer; S, switch; G, ground.

bridge, it was possible to avoid the difficulties which arise when the resistance ratio becomes very high, since voltmeter readings can be made on each side with approximately the same precision. Their ratio, whether large or small, can now be obtained to a considerable degree of accuracy. Since it was necessary to vary these potentials, the voltage on the high resistance side of the bridge was arranged so that it could be controlled with a point switch. A potentiometer which made possible an accurate voltage adjustment was used on the low resistance side of the bridge.

The operation of the bridge may be described as follows: A standard resistance is inserted at R. Then, after the introduction of the unknown resistance, μ, the voltages are varied until there is no swing on the electrometer when the electrometer switch S is opened. The bridge is now balanced, and the resistances stand as follows:

$$\mu/R = V_2/V_1 \quad \text{or} \quad \mu = V_1/RV_2$$

The voltages V_1 and V_2 are those read from the voltmeters, and R is the standard known resistance. Good results may be obtained when the ratio of the voltages, and therefore of the resistances, becomes as high as 1000 to 1. At this ratio there is still sensitivity in the arrangement to permit of an accuracy which will be limited only by the precision with which the two voltages may be read. Calibration of high resistance standards is necessary for the work with dielectric materials. A low resistance standard is inserted at R, with a higher resistance at μ. The resistance of μ is then determined by bringing the bridge to a balance. It may then be used as the standard for the next step. This may be continued until a standard is obtained that has a high enough resistance for the range of measurements that are to be made.

The highest standard used had a resistance of 2440 megohms, which makes possible the measurement of a resistance of approximately 1.6×10^{13} ohms. It would be possible, of course, to go to higher resistances with a higher standard resistance, but at the higher resistances the static effects become appreciable and make measurements more difficult. In such cases the operator of the bridge must remain quiet while making a reading; otherwise the electrometer may swing back and forth, making an accurate balance impossible. The part of the wiring in the neighborhood of the points A, B, and C in figure 1 is that part which is the most sensitive to capacity effects. All metal parts were connected to a special outside ground whenever this was possible. It will also be appreciated that the operation of the bridge becomes difficult when the humidity is high.

The specific volume conductivities of ten substances, including six synthetics and four varieties of wood have been determined as a function of temperature. The synthetics include transparent Bakelite, ordinary black panel Bakelite, Du Pont Pyralin No. 1735, Glyptal resin, and two sorts of the resin known as "Beetleware" (No. 3 and No. 20), while the woods include birch, mahogany, red oak, and Sitka spruce. An attempt was made to measure the conductivity of hard rubber, but the conductivity was too low to be measured with the present apparatus at any temperature to which the rubber could safety be heated. All the synthetics were the usual commercial products, with the exception of the sample of Glyptal. The latter was prepared by us from glycerol and phthalic acid. After the cooking process had been completed the resin was cured in an oven kept at 120°C. for three days and at 150°C. for seven days. The conductivities of the woods were those of the woods in the dry state, as well as it could be attained. Before being used for the conductivity measurements the wood samples, cut as described in the next section, were kept at 105°C. in a dry kiln for several weeks, and during the measurements there was always a dish of anhydrous sulfuric acid in the constant temperature oven in which the samples whose conductivities were being measured were placed. The synthetics were kept in a sulfuric acid desiccator until they were taken out for measurement. The wood was apparently dry, since when the temperature of measurement was carried to 110°C. no break in the conductivity curve appeared.

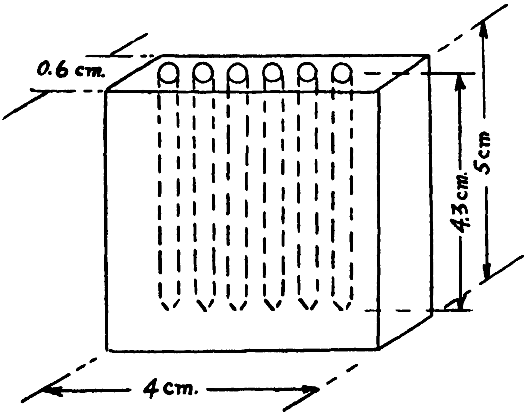

FIG. 2. CELL TYPE A

Electrodes formed by filling ⅛ inch holes, drilled with centers 0.5 cm. apart, with mercury. Alternate pools of mercury connected to form two electrodes.

Two types of conductivity cell were used. The cell of Type A is shown in figure 2. The woods, the panel Bakelite, and the Glyptal samples were cut to the shape of cells of this form. The wood samples were so cut that the conductivity was measured in a tangential direction relative to the direction of the grain. It would be very difficult to calculate the cell constant for such a cell with any degree of accuracy, so that it had to be obtained experimentally using a substance of known resistance. The apparent resistance was determined with the apparatus and the cell constant calculated. A sample of Bakelite AM-250, having a specific volume resistance of 8 × 10^9 ohms at 20–21°C., was the substance used as standard. All cells of Type A were made to have exactly the same dimensions. The conductivity of an unknown sample in this form was 168 times that of a centimeter cube. This constant probably should not be expressed to more than two significant figures, since the accuracy of the measurements of the conductivity of the Bakelite standard was given as 1 per cent, and since it is difficult to reproduce exactly the dimensions of the standard Bakelite cell in the other dielectrics.

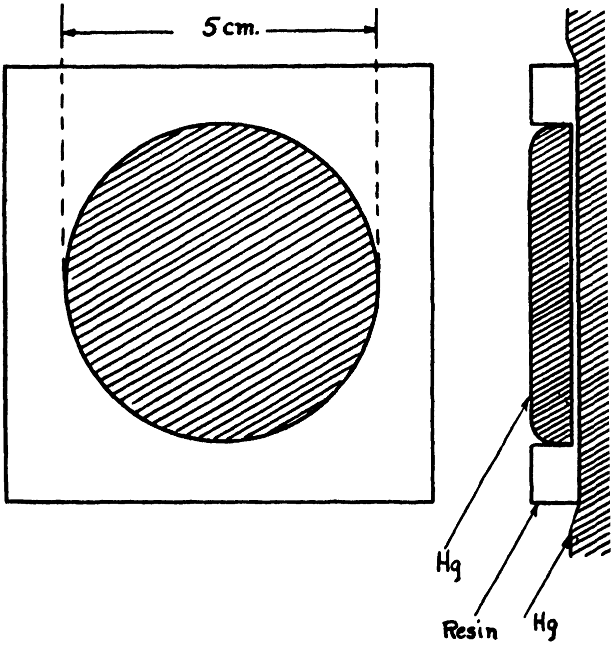

FIG. 3. CELL TYPE B
Uses mercury electrodes as indicated

The type B cell is shown in figure 3. The cell constant in this case was calculated from the diameter of the hole turned in the sample, and from the thickness of the bottom, as measured by a micrometer caliper. It was necessary to assume in this case that the part of the current which did not flow directly through the bottom from the inside mercury pool to the outer mercury was negligible. Measurements were made on the Pyralin, transparent Bakelite, and Beetleware samples using this type of cell.

An attempt was made in all cases to reduce the surface conductance to a minimum. The cells were so designed that this conductance would be as low as conveniently possible. It has already been mentioned that a dish of anhydrous sulfuric acid was always present when measurements were being made. Since the measurements were taken over a considerable range of temperature, and since there were no irregularities in the curves in passing from below 100°C. to higher temperatures, it is believed that the data given relate essentially to volume conductivity. In all cases the potential V_2 was applied to the sample for at least an hour before any measurements were taken, in order to reduce dielectric absorption effects to a small quantity.

During the course of the experimental work it was noted that the results could not be reproduced with any considerable degree of precision. The curves were only partially reversible, since either the composition or structure of the materials appeared to change irreversibly with increasing temperature. Experiments with different samples of one and the same substance did not give absolutely the same conductivity, though the differences were never great. Samples cut from the same section of a given material varied only slightly from one another, probably owing to unavoidable inaccuracies in the reproduction of the dimensions of the test cells.

EXPERIMENTAL RESULTS

As typical of the experimental results, conductivity data for one wood (birch) and one synthetic (Black panel Bakelite) are presented. The columns of the tables indicate, from left to right: the Centigrade temperature, the absolute temperature, values for the quantity $\mu = V_1/RV_2$ (R is the resistance of the standard used to obtain the balance), the numerical value of the conductivity represented by the quantity μ, the specific volume conductivity, its logarithm, and the reciprocal of the absolute temperature. These data are also presented as graphs (figures 4 and 5), in which the logarithm of the specific volume conductivity is plotted against the reciprocal of the absolute temperature. It is evident that the data are well represented by straight lines. This was true in the case of all substances investigated, with the possible exception of the sample of Glyptal resin, in which case the slope of the curve became somewhat less steep as the temperature was increased.

Because of the interest in a comparison of the relative ability of these substances to resist the passage of the electric current at ordinary temperatures, table 3 has been prepared. The specific volume conductivities at 20°C. have been obtained by extrapolation of experimental curves. In the cases of the Glyptal resin and of the woods this extrapolation is somewhat long (over a temperature interval of 50°C.), nevertheless the value as given is believed to represent the proper order of magnitude. There have also been included in this table values for E, a quantity which we shall call

TABLE 1

Birch wood. Conductivity in tangential direction

Cell Type A. Cell constant = 168.

Standard resistance B = 2440 megohms.

T	T	$\frac{V_1}{RV_2}$	μ	$\bar{\mu}$	LOG $\bar{\mu}$	$1/T$°K.
°C	°A.					
68	341	$\frac{0.040}{249B}$	6.59×10^{-14}	3.91×10^{-16}	*16*.59	0.00293
74	347	$\frac{0.060}{249B}$	9.88×10^{-14}	5.86×10^{-16}	*16*.77	0.00288
80	353	$\frac{0.095}{249B}$	1.56×10^{-13}	9.28×10^{-16}	*16*.97	0.00283
84	357	$\frac{0.150}{249B}$	2.47×10^{-13}	1.47×10^{-15}	*15*.17	0.00280
87	360	$\frac{0.206}{249B}$	3.39×10^{-13}	2.01×10^{-15}	*15*.30	0.00278
91	364	$\frac{0.290}{249B}$	4.78×10^{-13}	2.83×10^{-15}	*15*.45	0.00275
110	383	$\frac{0.687}{124B}$	2.27×10^{-12}	1.35×10^{-14}	*14*.13	0.00261

TABLE 2

Black panel Bakelite

Cell Type A. Cell constant = 168.

Standard resistances D = 6.55 megohms, A = 43,300 ohms.

T	T	$\frac{V_1}{RV_2}$	μ	μ	LOG $\bar{\mu}$	$1/T$°K.
°C.	°A.					
21	294	$\frac{0.406}{262D}$	2.37×10^{-10}	1.41×10^{-12}	*12*.15	0.00340
26	299	$\frac{0.640}{262D}$	3.74×10^{-10}	2.22×10^{-12}	*12*.33	0.00335
32.5	305.5	$\frac{1.025}{152D}$	1.03×10^{-9}	6.09×10^{-12}	*12*.79	0.00328
35	308	$\frac{1.155}{109D}$	1.56×10^{-9}	9.26×10^{-12}	*12*.97	0.00325
38.5	311.5	$\frac{0.885}{44D}$	3.08×10^{-9}	1.83×10^{-11}	*11*.26	0.00321
46.5	319.5	$\frac{0.113}{262A}$	9.95×10^{-9}	5.91×10^{-11}	*11*.77	0.00313

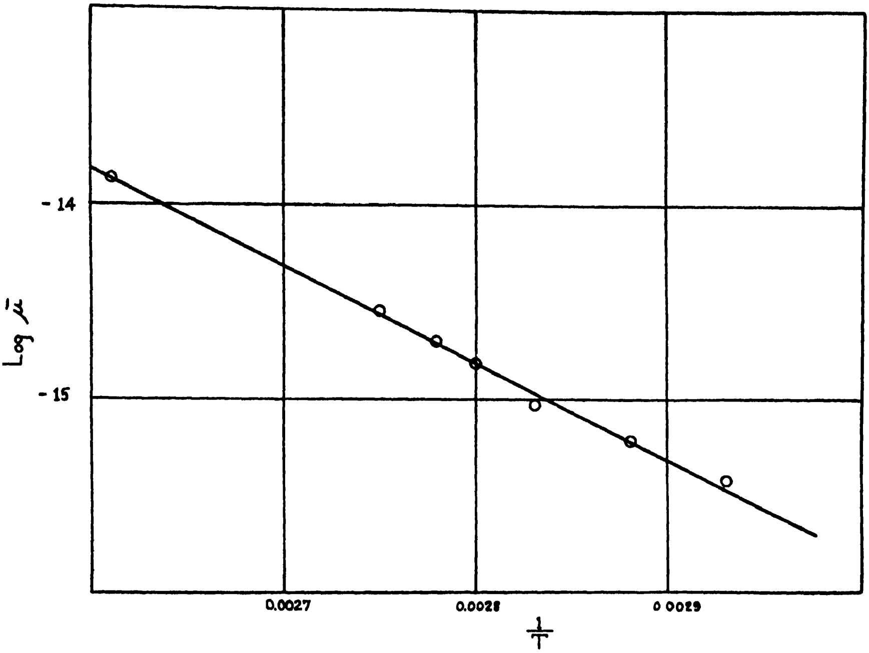

Fig. 4. Birch. Conductivity in Tangential Direction

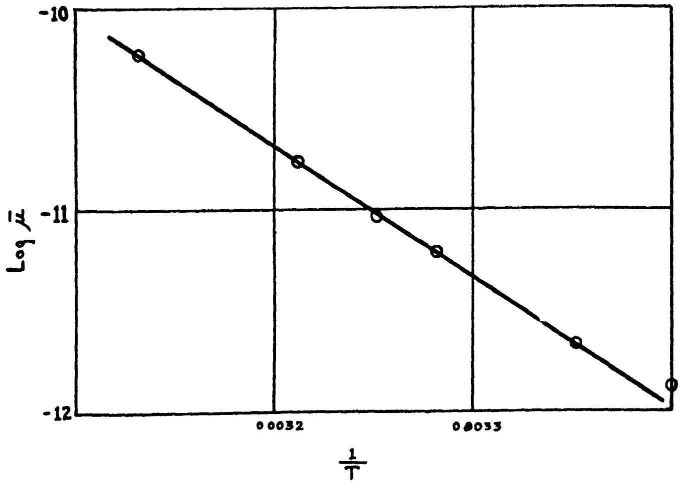

Fig. 5. Black Panel Bakelite

the energy of liberation of the carrier of the current. The significance of this quantity will be evident from the discussion to follow.

TABLE 3

Values of $\bar{\mu}$ and E for different materials

MATERIAL	$\bar{\mu}$ AT 20°C	E
		calories
Transparent Bakelite	$5\ 5 \times 10^{-16}$	37,500
Panel Bakelite	$8\ 5 \times 10^{-13}$	29,700
Beetleware No. 3 (blue)	$4\ 4 \times 10^{-15}$	42,500
Beetleware No 20 (black)	$6\ 0 \times 10^{-13}$	27,400
Pyralin	$2\ 6 \times 10^{-13}$	29,300
Glyptal	ca 1×10^{-23}	65,000
Birch	$1\ 2 \times 10^{-18}$	22,900
Mahogany	$3\ 7 \times 10^{-19}$	30,600
Red oak	$3\ 2 \times 10^{-19}$	28,400
Sitka spruce	$3\ 4 \times 10^{-18}$	32,000

DISCUSSION

It is believed that these conductivities and their variations with temperature could be explained as the result of an ionic process. The ions that carry the current appear to originate in the inevitable electrolyte impurities in the resins, and in the ionic impurities represented by the ash content of the wood. In the development of a mathematical relationship to express the conductivity as a function of temperature, the ions can be assumed to be distributed between two phases. There will be a certain number of ions adsorbed on the surface of the units of structure of the materials, and there will be another quantity in the free state between these units of structure, whose migration under the influence of the electric field causes a flow of current. This conductivity will be proportional to the number of free ions in any given substance, while the number of bound ions should not affect the simple conduction process. There will be an equilibrium at any given temperature between the free and the bound ions, thus

$$i_f/i_b = k \tag{1}$$

In this equation i_f and i_b are quantities which measure the concentrations of free and bound ions respectively, and k is a constant. Since the bound ions are in a phase distinct from that of the free ions, their concentration may be considered constant. Thus we may write

$$i_f = K, \quad \text{and} \quad K \sim \bar{\mu}, \tag{2}$$

where K is another constant, and $\bar{\mu}$ is the specific volume conductivity.

The general equation for the variation of an equilibrium constant with the temperature is

$$\frac{\mathrm{d} \ln K}{\mathrm{d}T} = \Delta H/RT^2 \tag{3}$$

where ΔH is the heat of an activation, R is the gas constant, and T is the absolute temperature. Assuming ΔH to be constant over the temperature range involved, this expression may be integrated, with the result

$$\ln K = -\Delta H/RT + c \tag{4}$$

where c is a constant of integration. Assuming equation 2 to be correct it follows that

$$\ln \bar{\mu} = -E/RT + C \tag{5}$$

where E is the energy of liberation of a mole of ions and C is another constant. If the logarithm of the specific volume conductivity is plotted against the reciprocal of the absolute temperature and a straight line results, the quantity E may be assumed to be constant. When Briggsian logarithms are used E may be calculated directly from the slope of this line, according to the equation

$$-E = \text{slope} \times 2.303\,R, \quad \text{or} \quad -E = \text{slope} \times 4.576 \tag{6}$$

When the logarithms of the observed conductivities are plotted against the reciprocals of the absolute temperature a straight line with a negative slope results. This is taken to indicate that as the temperature is increased ions are liberated from the surface of the micells to the free condition in an endothermic process, causing thereby an increase in the conductivity as the temperature is increased.

At this point it is of interest to recall briefly the explanations given for the conductivity of a simple crystal as a function of temperature. Smekal (10) and his followers believe that in the case of crystalline dielectrics in which there are ionic conductors, the mechanism is essentially bound up with the deviation of the actual crystal structure from that of the ideal lattice. The ions which take part in conduction are assumed to be concentrated in positions in the crystal where these lattice imperfections are present and to move in adsorbed and free condition along the paths formed by these crystalline fissures. On the other hand Joffé (9), Phipps (11), and others believe that the conduction in such cases is due to a volume process in which either one or both of the ions is liberated from its normal lattice position by the absorption of energy in the form of heat. They believe the conductivity to be a property of the chemical substance rather than of the crystal and that it is independent of crystal imperfections. Thus, for sodium chloride Phipps, Lansing, and Cooke give for the quantity corresponding to our E the value 20,200 calories. It is defined as the heat of liberation of a gram ion in the crystal lattice, that is, the work necessary to produce a mole of ions (in this case, positive) in the interior of a crystal. As indicated in the introduction, there are certain types of crystal (sulfides, oxides) in which the conduction process may be electronic in nature.

Similar possibilities present themselves in the case of the materials in question and it will be equally difficult to decide between them. Amorphous dielectrics with electrolyte impurities may show increasing conductivity with temperature because ions are continually liberated from salts contained within them or because ions already present are removed from the inner surfaces to which they are adsorbed to the more mobile condition that we have described as free. It may be remarked that the presence of moisture is not necessary for the existence of an appreciable number of ions within a dielectric, since the electrolyte impurities present are already in the ionic form. It is true that dielectrics usually contain some water, the last traces of which are almost impossible of removal, so that dissolved salts will be ionized in solution but dissolved ions will tend to concentrate in the bulk of the water solution rather than at the interfaces, because salts as a class are capillary inactive. We have derived the mathematical relationship between conductivity and temperature assuming an equilibrium between the free and bound ions. However, we might also have derived an equation of the same form on the assumption that the amorphous dielectrics act, as far as the process of electrical conduction is concerned, in the same manner that Joffé and Phipps have explained the conductivity of a sodium chloride crystal. In this case we should have dealt with what might be termed a "dilute crystal," since relatively large volumes of inert materials would be present along with the electrolyte materials. An electronic process seems less probable in the case of amorphous materials, though it should not be excluded as a possibility without further information.

In view of the difficulties involved in a differentiation between the mechanisms which have been proposed to account for the conduction through a simple crystal, it is evident that one cannot hope to decide between the possibilities mentioned for the amorphous substances with the meager data now available. This assignment of a mechanism is rendered more difficult because the general form of the mathematical expression for the conductivity as a function of temperature will apparently be the same in the several cases. Nevertheless it is of interest that the conductivities of all the amorphous materials studied increase with the temperature according to a well-known physico-chemical law. It is hoped that further experiments with these substances containing known amounts of added electrolyte material will advance our knowledge of the conduction process taking place within them.

SUMMARY

There have been determined the specific volume conductivities of ten "amorphous" substances as a function of temperature. They include six synthetics and four varieties of wood. The resistances were determined by means of a modified Wheatstone bridge which has several advantages over the usual forms of apparatus for this type of work The specific volume conductivity, $\bar{\mu}$, changes with absolute temperature, T, according to the law,

$$\mu = k\, e^{-\frac{E}{RT}}$$

where E is an energy of liberation of the carrier of the current in calories, and k is a constant having the same dimensions as μ Possible mechanisms of the conduction process are briefly discussed.

REFERENCES

(1) Curie Ann chim phys [6] **18,** 203 (1889)
(2) Campbell Proc Phys Soc London, **25,** 336 (1912–3)
(3) Koenigsberger and Reichenheim Physik Z **7,** 570 (1906)
(4) Rasch and Hinrichsen Z Elektrochem **14,** 41 (1908)
(5) Pirani and Siemens Z Elektrochem **15,** 969 (1909)
(6) Dietrich Physik Z **11,** 187 (1910)
(7) Curtis Bur Standards Bull **11,** 359 (1915)
(8) Saegusa Science Repts Tôhoku Imp Univ , First Ser , **15,** 795 (1926)
(9) Joffé The Physics of Crystals McGraw-Hill Book Company, New York (1928)
(10) Smekal Z Elektrochem **34,** 472 (1928), Z Physik **56,** 579 (1929)
(11) Phipps, Lansing, and Cooke J Am Chem Soc **48,** 112 (1926)

THE AUTOXIDATION OF STANNOUS CHLORIDE. II

A SURVEY OF CERTAIN FACTORS AFFECTING THIS REACTION[1]

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The autoxidation of stannous chloride has recently been investigated by Filson and Walton (1), who studied the effect of hydrochloric acid on the reaction velocity and showed a linear relation between the velocity and the hydrogen-ion concentration. This paper is a continuation of the above work and is a general survey of certain factors influencing the rate of reaction.

APPARATUS AND PROCEDURE

Twenty-five cc. of an acid solution of stannous chloride were placed in a 150-cc. Pyrex flask of the type used by Filson and Walton. The flask was placed in a thermostated shaking apparatus and connected to a water-jacketed burette containing oxygen gas at the temperature of the thermostat, 25°C. When the system had come to constant temperature, the shaking apparatus was started and readings were taken on the volume of oxygen absorbed. The speed of shaking was selected as about 1000, since Filson and Walton had shown that higher speeds have no effect on the reaction velocity.

REAGENTS AND SOLUTIONS

Several brands of stannous chloride were used and were found to give varying results. Baker's "purified" salt gave results which were only slightly changed by three recrystallizations under nitrogen from hydrochloric acid solution, consequently this preparation was used in the experimental work. Solutions made from stannous chloride which had been dehydrated by treatment with excess acetic anhydride and washed with anhydrous ether (2) gave results which agreed with those obtained from the recrystallized hydrated salt.

The solutions, made in 2-liter batches and stored under nitrogen, contained approximately 32 grams of stannous chloride per liter, and were about 0.8 N in total hydrochloric acid (free acid plus that obtained by complete hydrolysis).

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Table 1 gives the data for the solutions used in this work.

ORDER OF THE REACTION

By neglecting the first 80 to 120 minutes of the run, during which the absorption was not always reproducible, a value of K (K = milligrams of oxygen absorbed per minute) was obtained which corresponds to a zero order reaction, within an experimental error of 5 to 7 per cent in the course of a 4 to 5 hour run. This neglected period corresponds to about a 10 per cent absorption of the theoretical amount of oxygen required to oxidize the sample completely. Duplicate runs for solution No. 6 are given in table 2, this solution having an average value of K of 0.0572 mg. per minute. The 5 to 7 per cent drop in the value of K can be attributed to a decrease in the concentration of the free hydrochloric acid, since this substance is used up during the oxidation of the stannous chloride. Some hydrochloric acid will be available through hydrolysis of the stannic chloride, but since the complex equilibrium between Sn^{++}, Sn^{++++}, HCl, and complex chloro acids is not fully known it is impossible to define the system definitely.

TABLE 1

Composition of the stannous chloride solutions

SOLUTION NUMBER	SOURCE OF $SnCl_2$	$SnCl_2$	HCl (TOTAL)
		grams/liter	*Normality*
5	Baker's Purified	36 5	0 783
6	Baker's Purified	31 3	0 758
7	Baker's Purified	31 7	0 733
8	Mallinckrodt's C P	35 5	0 814
9	General Chemical Co C P. (dehydrated by acetic anhydride)	32 6	0 782
10	Mallinckrodt's C P. (dehydrated by acetic anhydride)	32 7	0 811
11	Baker's Purified	33 6	0 840
12	General Chemical Co C.P. (recrystallized three times)	33 1	0 815

EFFECT OF TEMPERATURE

Runs were made on solution No. 12 at different temperatures. It was impossible to calculate values of K for comparison, since the apparent order of the reaction varied with the temperature. This change can be attributed to several factors. First, the solubility of oxygen is higher at the low temperatures, allowing a higher saturation concentration of oxygen, and thus increasing the reaction rate. Then, too, the change of temperature affects the equilibrium between Sn^{++}, $SnCl_2$ and the chloro acid complexes. These factors mask the true temperature coefficient of the reaction, so that the results are of qualitative importance only. The results

TABLE 2

Data for duplicate runs at 25°C.

Solution No 6

Stannous chloride, 31 3 grams per liter; hydrochloric acid (total) 0 758 *N*

TIME	RUN 165		RUN 168	
	Oxygen absorbed	*K*	Oxygen absorbed	*K*
minutes	*milligrams*	*mg /min*	*milligrams*	*mg /min*
10	0 60	0 0600	0 60	0 0600
20	1 17	0 0587	1 19	0 0593
30	1 77	0 0592	1 78	0 0594
40	2 35	0 0587	2 35	0 0587
50	2 87	0 0575	2 93	0 0587
60	3 48	0 0581	3 55	0 0591
70	4 01	0 0572	4 07	0 0581
80	4 56	0 0570	4 67	0 0583
90	5 10	0 0567	5 20	0 0578
100	5 67	0 0567	5 77	0 0577
110	6 19	0 0562	6 27	0 0570
120	7 29	0 0556	7 42	0 0570
140	7 86	0 0562	7 97	0 0570
150	8 37	0 0559	8 51	0 0567
160	8 96	0 0560	9 10	0 0568
170	9 48	0 0558	9 63	0 0568
180	10 06	0 0559	10 21	0 0567
190	10 70	0 0562	10 80	0 0568
200	11 19	0 0559	11 37	0 0568
210	11 75	0 0559	11 93	0 0568
220	12 31	0 0559	12 48	0 0567
230	12 89	0 0561	13 07	0 0568
250	13 91	0 0556	14 11	0 0566
270	15 00	0 0555	15 23	0 0565
		Av = 0 0568		Av = 0 0576

are expressed in terms of the time required to oxidize one-half of the stannous chloride, starting at the beginning of the run. From the curves in figure 1, the following "half-times" were interpolated:

At 45°C	144 minutes
35°C.	228 minutes
25°C.	320 minutes
15°C.	384 minutes
0°C.	330 minutes

The solubility of oxygen between 15° and 0°C. shows a marked increase, and this is probably the cause of the decrease in the time of half absorption for the lower temperature.

EVIDENCE FOR A CHAIN REACTION

A number of tests were made to determine whether or not there is any evidence that the reaction under consideration belongs to the chain type of reaction similar to the oxidation of sodium sulfite studied by Alyea and Bäckström (3).

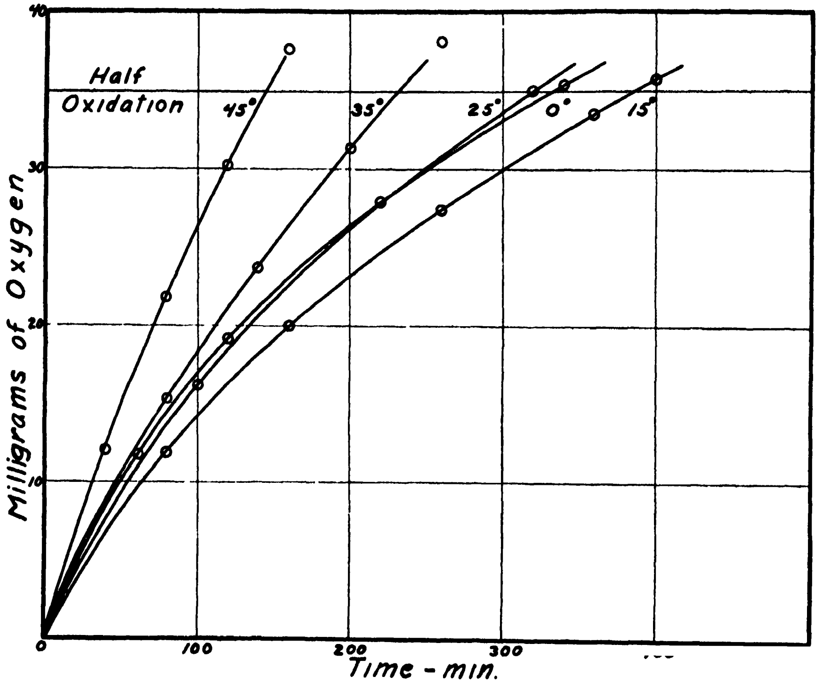

FIG. 1. THE EFFECT OF TEMPERATURE ON THE RATE OF OXYGEN CONSUMPTION BY STANNOUS CHLORIDE

This reaction meets the criterion of being exothermic, as was shown by Berthelot (4), whose work was done at 500°C. A confirmatory experiment in our laboratory, at room temperature, also indicated that the reaction is exothermic.

For the purpose of confirming the chain mechanism, tests were made on: (1) the influence of light; (2) the existence of an intermediate peroxide; (3) the effect of added substances, especially inhibitors; (4) the coupled oxidation of a second molecular species present in the system.

1. Effect of light

Visible light had no effect on the reaction rates. Two flasks were painted black, and the runs made in these showed no difference from those in unpainted flasks. In addition, some experiments were made in which a 250-watt tungsten light was placed adjacent to the reaction flask, and other experiments in which the direct beam of the strong green and yellow light from a high intensity capillary mercury vapor lamp was used. In both cases no acceleration of the reaction was noted. It was discovered, however, that ultra-violet light of wave length below 3070Å. was absorbed completely by the solution and that it speeded up the reaction very considerably. The details of these experiments will be discussed in a subsequent paper.

2. Detection of peroxide

A sample of the partially oxidized stannous chloride was found to give a peroxide test with titanium sulfate. This test could not be obtained after the solution had been allowed to stand for 2 or 3 hours, showing that the peroxide had been used up by reaction with more stannous chloride. No attempts were made to isolate the peroxide, because of the small amount present and its relative instability.

3. Catalytic effects of certain substances

One of the most important of the criteria of photochemical chain reactions, which can also be applied to thermal chain reactions, is the great effect of negative catalysts. The reaction of stannous chloride with molecular oxygen is very sensitive to the action of added substances, as shown both by our work and by that of Young (5). In attempting to duplicate Young's work on inhibition by alkaloids, it was found that cocaine, morphine, and brucine had little effect in 0.001 *M* solution. In 0.01 *M* solution a reduction to about 90 per cent of the normal rate was shown, and in a saturated solution, a reduction of 55–65 per cent of the normal values.

Because of the effect of the alkaloids it was of interest to investigate the action of other nitrogen compounds; accordingly a series of experiments was carried out in which many varieties of these compounds were used. The results are shown in table 3, in which the value of K is given, together with the percentage value of K in relation to the uncatalyzed value of K for the stock solution used in each experiment. It will be noticed that nitrogen compounds, in general, were inhibitors, but that the inhibiting power is affected by the position of the nitrogen and the nature of the other atoms bound to it. Amino compounds had little effect, some of them slightly inhibiting the reaction and some accelerating it slightly. Nitro compounds were the most effective of the inhibitors studied, and the mole-

TABLE 3

The effect of certain nitrogen compounds

Normal K values for the solutions: No. 5, K = 0.0626; No. 6, K 0.0572; No. 7, K = 0.0583 mg. per minute

SOLUTION	CONCENTRATION	COMPOUND	K	PER CENT OF NORMAL
		Alkaloids		
	moles/liter		*mg/min*	
5	0.001	Cocaine hydrochloride	0.0620	
5	0.001	Brucine	0.0574	91.7
5	0.1	Brucine	0.0345	55.1
5	0.01	Morphine hydrochloride	0.0565	90.3
5	0.1	Morphine hydrochloride	0.0407	65.0
5	0.01	Nicotine	0.0622	
6	0.01	Veronal	0.0552	96.5
		Nitro compounds		
6	0.01	*p*-Nitrotoluene	0.0112	19.6
6	0.001	Nitronaphthalene	0.0147	25.7
7	0.01	Nitromethane	0.0114	19.6
6	0.001	*o*-Nitrophenol	0.0106	18.6
7	0.01	*p*-Nitrophenol	0.0156	26.8
6	0.01	*m*-Nitroaniline	0.0012 to 0.0043*	About 5
6	0.001	*p*-Nitrobenzoic acid	0.0120	21.0
6	0.001	Nitrophenylhydrazine	0.0119	20.8
6	0.01	*m*-Dinitrobenzene	0.0029	5.1
6	0.001	*sym*-Trinitrobenzene	0.0081	14.2
6	0.01	Trinitrotoluene	0.0058	10.1
6	0.00001	Picric acid	0.0330 to 0.0444	About 60
6	0.0001	Picric acid	0.0170	29.7
6	0.0005	Picric acid	0.0154	26.9
6	0.001	Picric acid	0.0122 to 0.0179	About 25
6	0.01	Picric acid	0.0145	25.3
		Amino and imino compounds		
5	0.01	Glycine	0.0631	
5	0.01	*p*-Toluidine hydrochloride	0.0564	90.1
5	0.01	Phenylhydrazine hydrochloride	0.0382	61.0
6	0.01	Carbazole	0.0535	93.5
6	0.01	Hydroxylamine hydrochloride	0.0582	
6	0.01	Urea	0.0595	
7	0.002	Thiourea	0.0656	112.5
7	0.0045	Thiourea	0.1120	192.0
7	0.01	Thiourea	About 1.2	2060.0

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* The two values of K in some experiments denote a rise in the value of K, due to the destruction of the inhibitor.

TABLE 3—*Concluded*

SOLUTION	CONCENTRATION	COMPOUND	K	PER CENT OF NORMAL
		Amino and imino compounds—*Concluded*		
	moles/liter		*mg/min.*	
7	0.01	Ammonium thiocyanate	0.0465	79.8
7	0.01	Sulfanilic acid	0.0584	
7	0.01	Acetanilide	0.0571	.
7	0.01	Semicarbazide hydrochloride	0.0501	85.9
7	0.01	*p*-Aminophenol	0.1028	176.3
		Other nitrogen compounds		
6	0.001	Cellulose nitrate	0.0470	..
7	0.01	Potassium nitrate	0.0564	96.7
7	0.01	Potassium cyanide	0.0517	88.7
7	0.01	Butyl cyanide	0.0536	91.9
7	0.01	Acetoxime	0.0567	97.3
7	0.01	Azobenzene	0.0208 to 0.0298	About 45
7	0.001	Aminoazobenzene	0.0587	
7	0.01	Aminoazobenzene	0.0642	110.0
7	0.01	Butyl nitrite	0.0576	
7	0.01	Azoxybenzene	0.0523	89.7
7	0.01	Guanidine nitrate	0.0421	72.2

cules with two or three nitro groups were more effective than those with one. In contrast with this, organic and inorganic nitrate salts showed little or no effect. The azo and hydrazine groups were fair inhibitors, while the cyanide, oxime, azoxy, amino, and nitrite groups had very slight inhibitory power, or none at all.

In general no attempt was made to discover whether or not the catalyst, either positive or negative, had been destroyed during the course of the reaction. In the case of picric acid the strong yellow color disappears during the course of the oxidation, and at the same time, a rise takes place in the rate of oxidation. Both of these facts indicate that the picric acid is destroyed during the reaction.

Thiourea is a marked exception to the other nitrogen compounds since it showed a strong acceleration of the oxidation in concentrations as low as 0.002 *M*. As the concentration was increased the amount of acceleration of the reaction increased, until at 0.01 *M* the initial rate was about 1750 per cent of the uncatalyzed value. However, at this concentration the rate of oxidation drops off rapidly, indicating that the thiourea is being destroyed. In studying the action of thiourea, two special runs were made, one using 0.01 *M* thiourea in 0.8 *N* hydrochloric acid, and the second similar, except for the addition of a small amount of stannous chloride

(0.007 M). In the first case, no absorption was noticed, indicating that under these conditions thiourea alone does not absorb oxygen. In the second run oxygen was absorbed until the stannous chloride was used up, when the absorption stopped. The accelerating action of thiourea is apparently due to the sulfur atom, since amino compounds have been shown to have little effect, and yet this action is very specific since some of the other sulfur compounds used had no effect (benzyl sulfide, sulfanilic acid, benzenesulfinic acid, and powdered sulfur). Some sulfhydryl compounds were used, such as cysteine, thiocresol, thiobarbituric acid, and thiosalicylic acid. These were all inhibitors, reducing the rate to 40–45 per cent of its normal value. Thioglycollic acid however had practically no effect on the rate. This is in agreement with Schöberl's work (6) in which he found a negative catalytic effect with cysteine and glutathione on the autoxidation of leuco methylene blue, but is opposite to the accelerating effect of sulfhydryl compounds in biological phenomena (7).

The oxygen compounds used had little effect The aliphatic alcohols increased the absorption rate 5 to 10 per cent and phenol had no effect, but hydroquinone, pyrogallol, and mannite decreased the value of K to about 90 per cent, and quinhydrone to 67 per cent of its uncatalyzed value. Other oxygen compounds, of widely different types—acids, ketones, thymol, ethyl ether, benzoyl peroxide, and paraformaldehyde—showed no appreciable effect on the rate of absorption.

Tetraethyllead gave a value for K of 455 per cent of the uncatalyzed value. Ammonium thiocyanate was a good inhibitor; potassium cyanide, potassium nitrate, benzene, and anthracene decreased the value of K, 5 to 15 per cent. Certain other compounds had no effect; this group includes arsanilic acid, magnesium chloride, magnesium pyrophosphate, dibasic sodium phosphate, sodium arsenate, sodium pyrophosphate, and mineral oil. Silica gel, ground to 180 mesh, had no effect on the rate, showing that the reaction does not take place on the surface of the flask, but is a true solution reaction.

Catalysis by charcoal

The catalytic acceleration of many autoxidations by charcoal suggested its use in this study. Powdered willow charcoal accelerated the reaction but not in proportion to the weight used. For example, 0.12 mg. per cc. increased the rate to 167 per cent of its normal value; 0.6 mg. per cc. increased it to 228 per cent; and 1.2 mg. per cc. increased it to 253 per cent. This differs from the results of Lamb and Elder (8) who found for autoxidation of ferrous sulfate that the increase in oxidation rate was proportional to the amount of charcoal used.

As in other autoxidations in which charcoal has been used it was found that the "active centers" on the charcoal can be promoted or poisoned.

Promotion was shown by copper salts. The initial absorption rate for charcoal alone was 1.72 mg. per 10 minutes, for cupric chloride alone, 2.01 mg. per 10 minutes, while cupric chloride and charcoal together gave a value of 10.80 mg. per 10 minutes. These values are given in grams, since a value of K could not be calculated for the promoted catalyst.

The poisoning effect was shown by picric acid and by sodium arsenate. The latter compound had no effect on the reaction rate when used alone; charcoal alone increased the rate to 228 per cent of normal, but when the two were used together the rate was reduced to exactly the uncatalyzed value. This is similar to the results of Lamb and Elder (8), in which they found that phenylurea, amyl alcohol, and acetanilide when used alone showed no effect on the autoxidation of ferrous sulfate, but that they destroyed the accelerating influence of charcoal on the reaction. Picric acid showed a strong inhibition for the stannous chloride reaction, and when it was used in conjunction with charcoal, absorption rates were obtained which lay between the values for the two substances singly. According to the Taylor theory (9) these compounds are preferentially absorbed at the most active points and prevent the usual accelerating action of the charcoal.

4. Coupled oxidation

It was found that while an aqueous solution of allyl alcohol does not absorb oxygen, there is coupled oxidation of the allyl alcohol in the presence of stannous chloride. In order to determine the amount of excess absorption, the apparatus was arranged so that solid stannous chloride could be held above the solution in a glass capsule until the gas had come to constant temperature. The capsule was dropped into the acid solution with the first shake of the machine. In this way, it was possible to measure the total amount of oxygen absorbed by the system. By using pure oxygen as the atmosphere, the experiment was completed in a short time. Table 4 gives the results of this work, showing the effect of varying amounts of stannous chloride, allyl alcohol, and acid. The effects of temperature and of added substances are also given. The per cent excess absorption increased with increasing amounts of allyl alcohol, and decreased with increasing amounts of stannous chloride and hydrochloric acid. These effects may be explained by the assumption that the allyl alcohol is oxidized by the primary peroxide. With increased concentration of allyl alcohol more of the chains will involve alcohol molecules, and thus a larger amount will be oxidized.

Increased amounts of stannous chloride or hydrochloric acid cause an increase in the rate of consumption of oxygen, and at the same time cause a decrease in the amount of induced oxidation. Increased temperature, and homogeneous catalysts such as cupric chloride and thiourea, also have

TABLE 4

Induced oxidation of allyl alcohol

(a) Effect of varying amounts of stannous chloride

0 854 gram allyl alcohol in 25 cc. of 0 440 *N* HCl

$SnCl_2$	EXCESS O_2 ABSORBED
grams	*per cent*
0 127	45 1
0 381	34 8
0 635	28 1

(b) Effect of varying amounts of allyl alcohol

ALLYL ALCOHOL	EXCESS O_2 ABSORBED
(1) 0 381 gram $SnCl_2$ in 25 cc of 0 440 *N* HCl	
grams	*per cent*
0 171	19 4
0 854	34 8
1 708	36 2
(2) 0 635 gram $SnCl_2$ in 25 cc of 0 440 *N* HCl	
0 171	14 8
0 854	28 1
1 708	31 3

(c) Effect of temperature

0 381 gram $SnCl_2$ in 25 cc of 0 440 *N* HCl

ALLYL ALCOHOL	EXCESS O_2 ABSORBED		
	15°C	25°C	35°C
grams	*per cent*	*per cent*	*per cent*
0 085	16 8		
0 171	20 1	19 4	16 4
0 854	37 2	34 8	27 6
1 708	40 1	36 2	36 3

(d) Effect of additional substances with allyl alcohol

0 381 gram $SnCl_2$ + 0 171 gram allyl alcohol in 25 cc 0 440 *N* HCl

ADDED SUBSTANCE	EXCESS O_2 ABSORBED
	per cent
None	19 4
+0 1 gram thiourea	7 2
+0 1 gram charcoal	23 7
+0 1 gram $CuCl_2$	8 7

TABLE 4—*Concluded*

(e) Effect of acid

0.854 gram allyl alcohol; 0.381 gram $SnCl_2$

ACID	EXCESS O_2 ABSORBED
	per cent
None (25 cc H_2O)	28.1
10 cc. 0.440 N + 15 cc H_2O	44.4
25 cc 0.440 N	34.8
25 cc 4.0 N	7.7

TABLE 5

Induced oxidation in non-aqueous solvents

SOLVENT	SPEED OF REACTION	TOTAL GRAMS OF OXYGEN USED BY 0.320 GRAM OF ANHYDROUS STANNOUS CHLORIDE	EXCESS OXYGEN USED
			per cent
Ethyl alcohol	Rapid		About 50
Isopropyl alcohol	Rapid	0.04194	55.3
Amyl alcohol	Rapid	0.04450	64.3
n-Heptyl alcohol	Rapid	0.04777	76.9
Cyclohexanol	Rapid	0.04912	81.9
Benzyl alcohol	Slow		
Phenylethyl alcohol	Slow		
Cresol	Slow		
Acetic acid	Rapid	0.03585	32.3
Propionic acid	Rapid	0.04088	51.4
Ethyl acetate	Rapid	0.03169	17.4
Butyl butyrate	Rapid	0.03454	28.0
Acetone	Rapid		About 30
Acetophenone	Slow		
Aniline	Slow		
Pyridine .	Slow		
Dibutyl ether	Slow		
Glycerine	Slow		
Benzene	Very slow		

the dual effect of speeding up the rate of consumption and of decreasing the amount of induced oxidation. Charcoal, on the other hand, while it is also a positive catalyst, increased the amount of induced oxidation. This may be explained by the higher concentrations of allyl alcohol produced at the surface of the charcoal by adsorption.

Several other substances were used in place of allyl alcohol in investigating the phenomenon of induced oxidation. It was found that there was no excess oxygen used when acetone, phosphorus acid, maleic acid, or *p*-aminophenol were used, but that butyraldehyde used 14.8 per cent excess.

Coupled oxidation was also found when stannous chloride was oxidized in non-aqueous solvents. The solvents used are shown in table 5 together with the total grams of oxygen used and the per cent excess over the theoretical amount necessary for oxidation of the stannous chloride. There seem to be two classes or types of solvents among those tried, one class in which the oxidation is fast and the second in which it is slow. In the former group the oxidation of the sample was complete in 3 to 10 minutes, in spite of the fact that no excess hydrochloric acid was present as in the case of oxidation in aqueous solution. In each solvent of this group an excess of oxygen was used. In the rest of the solvents the reaction was comparatively slow, so that it was not followed to completion. There is no relation between the phenomenon of molecular compound formation and this division into types, for substances which form molecular compounds with stannous chloride are found in both classes. Neither is there a relation between ease of oxidation and the separation into types, since compounds which are easy to oxidize and others which are hard to oxidize are found in both classes.

DISCUSSION

The results of the foregoing experiments are best explained by the well-known peroxide theory of autoxidation, in which it is held that oxidations of this type are attended by the intermediate formation of metastable or dative peroxides which are characterized by high energy content and great instability. Such peroxides are very active and account for many of the phenomena of autoxidation (10). Mention has been made of the fact that in the autoxidation of stannous chloride enough peroxide is formed to be detected qualitatively. Further evidence of the existence of a peroxide is afforded by the induced oxidation of many compounds, especially alcohols.

That this reaction is a chain reaction is supported by the great influence of added substances, particularly inhibitors, on the course of the oxidation, and also by the fact that the reaction is exothermic. There is also further support from photochemical data.

In the autoxidation of stannous chloride there is reason to believe that a complex chloro acid is the form in which the Sn^{++} is oxidized. Prytz (11) has shown that the complex ions $SnCl_3^-$ and $SnCl_4^{--}$ exist in aqueous solutions of comparatively low hydrochloric acid concentration. This conclusion is supported by the fact that an excess of hydrochloric acid has a great accelerating action on the autoxidation of stannous chloride. Complexes are also known between stannous chloride and potassium chloride or sodium chloride, and these substances act in a manner similar to that of hydrochloric acid in accelerating the autoxidation of stannous chloride, but to a less degree than does hydrochloric acid. In another paper further evidence will be given to show that in the photochemical autoxidation the substance which actually absorbs the light quanta and becomes activated is a complex ion of this type.

SUMMARY

1 Increased temperature increases the rate of autoxidation of stannous chloride, but the true temperature coefficient is masked by the change in the solubility of oxygen and changes in the complex equilibria existing in the solution

2 Visible light has no effect on the reaction but ultra-violet light below 3070Å is absorbed and accelerates the reaction

3 A peroxide was detected in the fresh, partially oxidized sample of stannous chloride This peroxide disappears by reaction with further stannous chloride

4. Many organic substances, particularly nitro compounds, were found to be inhibitors of the reaction Picric acid was the strongest inhibitor found, and this inhibitor was shown to be destroyed during the oxidation

5 Thiourea was found to be a strong positive catalyst for the autoxidation

6 Poisoning and promoter action were found for the catalysis of the reaction by powdered willow charcoal

7 Coupled oxidation of a second molecular species was found in aqueous solution in the cases of allyl alcohol and butyraldehyde, and in many non-aqueous solvents such as alcohols, acids, esters, and ketones.

REFERENCES

(1) Filson, G W, and Walton, J H J Phys Chem **36**, 740 (1932)
(2) Stephen, H J Chem Soc **1930**, 2786
(3) Alyea, H N, and Backström, H L J J Am Chem Soc **51**, 90 (1929)
(4) Mellor, J W A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol 7, p 427 Longmans, Green and Company, London (1927).
(5) Young, S W J Am Chem Soc **23**, 119 (1901)
(6) Schoberl, A Ber **64**, 546 (1931)
(7) Milas, N A Chem Rev **10**, 295 (1932), especially p 312
(8) Lamb, A B, and Elder, L W, Jr J Am Chem Soc **53**, 137 (1931)
(9) Taylor, H S J Franklin Inst **194**, 1 (1922)
(10) Milas, N A Chem Rev **10**, 295 (1932), for an excellent review of autoxidation
(11) Prytz, M. Z anorg Chem **172**, 147 (1928)

NEW BOOKS

New Conceptions in Biochemistry. By N. R. Dhar. 23 x 16 cm.; pp. x + 168. Allahabad: The Indian Drug House.

In the preface the author says: "Since the days of Lavoisier, animal metabolism has been a fascinating subject of research for chemists and physiologists alike. Despite the attempts of numerous distinguished workers, the enigma of animal metabolism still remains unsolved. In this book an effort has been made to discuss the general physico-chemical principles underlying animal metabolism. The book deals with the chemical aspects of biochemistry which have any bearing on metabolism. It is therefore in no way to be a book of reference. No attempt has been made to describe systematically all diseased conditions occurring in cases of improper metabolism. The dominant idea in the book is that several diseases are due to a lack of a proper and balanced oxidation of the three classes of food materials, the carbohydrates, fats, and proteins."

The headings of the chapters are: an introduction to views on food principles and chemical aspects of metabolism; biological oxidations; carbohydrate metabolism; metabolism of fats; oxidation of mixtures of carbohydrates, fats, and proteins; actino-therapy; deficiency diseases, internal secretions, vitamins, and light; normal ossification, and the formation of crystalline deposits in diseases; gout, fever, and uses of alkali, phosphates, and iron preparations; acclimatization and physical interpretation of Rubner's law of surface—and the ageing of cells. catalysts, and body colloids—the problem of old age and death; coagulation of blood, serum, and milk.

"Oxidation is the central life process supporting the entire complicated machinery of the living being. The substances undergoing metabolism in the animal body, comprising proteins, carbohydrates, and fats, are entirely resistant to oxidation by molecular oxygen under ordinary conditions. Yet in the animal body they are oxidized with the greatest ease into their end-products," p. 14.

"It is evident that acetone bodies are not products of normal metabolism, but result from abnormal conditions. The author has suggested that under normal conditions, fats are mainly burned in the animal body directly to carbon dioxide and water, without the formation of intermediate products. An objection may be raised as to how a fatty acid containing 18 carbon atoms can be directly oxidized to carbon dioxide and water without the formation of intermediate products. Many physiologists are of the opinion that acetoacetic acid, with four carbon atoms in its molecule, undergoes complete oxidation to carbon dioxide and water. If a molecule with four carbon atoms can be directly oxidized, then the direct oxidation of more complex acids is not impossible," p. 41.

"In the absence of thyroid there is little oxidation of fat. When fat is being metabolized in the body, the oxidation of carbohydrate is retarded. From this it will be seen that in the cases of thyroid removal there will be rapid oxidation of glucose; added to this is the accelerating effect of insulin on glucose oxidation, if insulin is injected. Therefore, there will be a greater lowering of blood sugar in cases of thyroid removal than in cases where the thyroid is functioning normally. Hence the greater violence of symptoms following an overdose of insulin," p. 53.

"We have demonstrated that the oxidation of substances like sodium sulphite, ferrous hydroxide, etc., by air or oxygen is greatly retarded by the presence of sugars, sodium arsenite, etc., which in their turn, are oxidized in presence of sodium sulphite, ferrous hydroxide, etc. Similarly, we have proved that the oxidation of fats is retarded by carbohydrates and vice versa," p. 57.

"In the case of adrenal secretions, we assume that the oxidation of fat is also accelerated by the promoter action of the secretion, and consequently in this case also the main store of energy comes from the oxidation of fat, and so the glucose is not oxidized and glycosuria results.

"With pituitary the case is different; for we assume that in presence of this secretion it is mainly the oxidation of protein matter which is increased; and consequently the energy supply comes from this oxidation, leaving glucose and fats unoxidized. From this point of view it will be clear that the function of the pancreas secretion, which mainly accelerates the oxidation of glucose, need not be considered antagonistic to that of the thyroid, pituitary, or adrenals. We assume that the matter merely rests on the preferential oxidation of one variety of food material due to the presence of the promoter. In hyper-functioning of the pancreas the glucose will be readily oxidized, and will supply the energy Hence, according to our point of view, the pancreas need not inhibit the action of the thyroid, or the adrenals; moreover, the adrenal or thyroid need not inhibit the action of the pancreas. We are strongly of the opinion that in normal health pancreas, thyroid, adrenal, and pituitary perform their proper function by promoting the oxidation of carbohydrates, fats, and proteins in the proper proportions. Consequently a combination of the respective hormones, especially thyroid and pituitary, should yield better results in many diseases than either singly," p. 58

"Addison's disease is today regarded by most investigators as due to hypofunction of the adrenal glands. It develops gradually with general asthenia, lack of interest, and malaise; digestive disturbances are common, with vomiting or diarrhoea and constipation, which may be alternating in character. Addison's disease usually resists all methods of treatment. Organotherapy with adrenal substance offers great hope, and in the hands of numerous practitioners has proved far more effective than all other therapy," p. 86.

"Rohrig and Zuntz showed that a curarized warm-blooded animal at ordinary room temperature lost the power of maintaining its body temperature and that the intensity of metabolism decreased accordingly. Curare prevents the transmission of motor impulses to voluntary muscles. Krogh states that the curve of oxygen absorption as influenced by body temperature is the same in the anesthetized frog and fish as in the curarized dog," p. 123.

The author is attempting to show that many physiological disturbances are due to improper and unbalanced oxidation. The reviewer is attempting to show that many physiological disturbances are due to over-agglomeration or over-dispersion of proteins. Some day some intelligent person will show that these are two parts of the same point of view. Perhaps improper and unbalanced oxidation causes over-agglomeration or over-dispersion of proteins.

WILDER D. BANCROFT.

Physical Chemistry for Students of Biology and Medicine. By DAVID I. HITCHCOCK. 23 x 15 cm.; pp. xii + 182. Baltimore: Charles C. Thomas, 1932. Price: $2.75.

In the preface the author says: "The material presented in this book has been offered during the past five years to medical and graduate students in Yale University as a part of the course in physiology."

The chapters are entitled: gases; liquids and gases; solutions; solutions of electrolytes—the law of mass action; hydrogen ions, indicators and buffers; galvanic cells and electrometric pH determination; adsorption—the colloidal state; membrane equilibrium; equilibria in blood; reaction velocity and enzyme action; oxidation-reduction potentials—phase boundary of potentials; electrokinetic phenomena; transformation of energy.

The book is essentially orthodox. Distrubing facts are ignored conscientiously and effectively. No reference is made anywhere to the effect of solubility on partial pressures, as in the case of ether and water and consequently there is no reference to the absence of any solubility term in the so-called Raoult formula.

All proteins combine stoichiometrically with hydrogen chloride and albumin forms true solutions in water, p. 116.

Wilder D. Bancroft.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 59. Eisen. Teil A. Lieferung 4. 26 x 18 cm.; pp. 587-846. Berlin: Verlag Chemie, 1932. Price 41 Marks (Subscription Price 35.50 Marks).

This volume, written by Prof. Durrer of the Technische Hochschule, Charlottenburg, is a continuation of Lieferung A3, will be completed by Lieferung A4, and deals with the metallurgy of iron. It contains accounts of the puddling process, the Bessemer, Thomas and other Open-Hearth processes, electric furnace methods, and several minor processes. The references to the literature are very complete, including European and American publications, and there are numerous curves and illustrations of plant. The actual text is relatively meagre, most of the space being taken up by literature references, and numerical data, so that the volume is essentially intended for readers who have a good library available. It cannot replace the usual works on ferrous metallurgy, since the descriptions are far too sketchy to be of any particular value in themselves. It would seem that by branching off into chemical technology the editors of Gmelin have rather departed from the intention of the work, and if other parts of the subject are to be treated on the applied side in the same way as in the present volume, the result will be somewhat disappointing.

J. R. Partington.

Eisen- und Stahllegierungen Patentsammlung. Zugleich Anhang zur Metallurgie des Eisens in Gmelins Handbuch der anorganischen Chemie. By A. Grützner. 26 x 18 cm.; pp. 308. Berlin: Verlag Chemie, 1932. Price 32 Marks.

This volume, which is an appendix to the sections on iron and steel in Gmelin's Handbuch, consists entirely of references to patents, with brief statements of the contents, arranged in tabular form according to the chemical composition of the systems. The patents cover the period 1880 to 1932 and various countries, and there are 7000 references. There is no doubt that such a work will save an enormous amount of time and labour and the price must be considered reasonable. It should be in all technical libraries.

J. R. Partington.

The Sorption of Gases and Vapours by Solids. By J. W. McBain. 23 x 14 cm.; pp. xii + 577. London: Geo. Routledge and Sons, 1932. Price 25 shillings net.

The group of rather heterogeneous phenomena known as the sorption of gases and vapours by solids has been the subject of a great number of experimental and theoretical investigations, and has acquired an extensive and scattered literature. In view of the great general interest of the subject, a book merely giving a classified survey of the material and literature references would in itself be of appreciable utility, but when such a comprehensive treatment is accompanied, as it is in the present volume, by the critical and suggestive views of an expert, the book naturally becomes one of considerable interest and importance. In his book, McBain has provided not only workers in this field but also chemists and physicists in general with an account of the particular aspects of sorption indicated in the title which is likely to become the standard work of reference. The range of material dealt with is surprisingly large, and in his careful study of the literature, in the great majority of cases obviously in the original, the author has not only materially contributed to the attainment of a proper perspective but has also performed an exacting task for which he deserves the thanks of his readers. The literature references are very full, in a few cases the bibliography having been contributed by specialists, and the author index contains 1500 names. There is a short subject index and an index of substances, so that the use of the book for purposes of reference is easy. Numerous tables and curves are given in the text. In some cases the descriptions on the curves are in German, and some rather complicated diagrams of apparatus are not explained in the text.

The emphasis in the treatment is on the experimental side, although the theories are also discussed in a critical manner. For the detailed mathematical treatment of the theories the reader is referred to other works. The style is generally terse, sometimes even to the point of being in places rather difficult to understand, and the large amount of information given sometimes leads to a slight lack of coherence in the text, which makes the reading rather tedious. In compensation for this, the reader will find that the book covers a really amazing amount of ground and gives a well chosen selection of numerical data.

Among the contents are descriptions of the experimental methods; sorption by charcoal, zeolites, silica and other gels, glass, impermeable crystals, metals; the thickness of the adsorbed film; mobility in sorbed films; sorption by jellies; effect of sorption on the solid; heat of sorption; theories of sorption; contact catalysis; the electrical interpretation of sorption.

The author, as a result of his critical survey, concludes that Langmuir's theory of adsorption is the one which agrees best with all the available facts, although he admits that in some cases the same data have been used to support two conflicting theories. He claims (p. 459) that the condensed film theory has been disproved by some experiments by himself and Britton, but omits to mention that in the same issue of the journal in which these were published another set of experiments by Foote and Dixon were reported which, although not specifically designed to test that theory, were shown to be in agreement with it. The remarkable experiments of Hardy haunt the exposition of the monomolecular film theory in several places, and it is regrettable that the work of Bastow and Bowden came too late for inclusion.

The book is one which should find a welcome from many classes of readers and deserves the highest commendation. The great bulk of the literature might well have overwhelmed a less enthusiastic and energetic author, but McBain has not only mastered it but has been able to deal with it in a critical and suggestive manner which deserves great praise and adds materially to the value of the book.

J. R. PARTINGTON.

Wörterbuch der Kolloidchemie. By ALFRED KUHN. 19 x 13 cm.; pp. 179. Dresden: Theodor Steinkopff, 1932. Price RM. 8.

This book is not, as its title states, merely a dictionary of colloidal chemistry. The treatment lies between that adopted in a standard English dictionary and that in an encyclopedia, the more important topics being treated in greater detail; for example, the phenomenon of swelling is given over four pages, adsorption and its related phenomena in its general aspects, nine pages, while seventy-word paragraphs suffice for such subjects as the Hofmeister series, the smectic condition, and thixotropy The name of the author of the term is given wherever possible, and sometimes the full reference, and at the end is a useful list of the important books on various aspects of colloid chemistry

This book will satisfy a definite need at this time There is such a vast output of literature on the subject, and the terms used have multiplied at such a rate, that it is often difficult even for a worker in this field to keep track of the many terms which research workers so delight in introducing If colloid chemists have this difficulty, what must be the plight of those specializing in other branches—physicists, biologists, and technical scientists—when they encounter such terms as "eukolloid," "Pringheim's rule," "polyene" and "lyosorption?" A large number of these will, it is hoped, fall into disuse, and, indeed, one of the results of the publication of this dictionary should be a great simplification of colloid-chemical terminology

It is difficult to find any serious omissions in this volume It is inevitable that one wishes in one place for greater, and in another place for considerably less detail Dr Kuhn is to be congratulated sincerely on an achievement of very considerable value to colloid chemistry

D C Jones

Die Industrielle Herstellung von Wasserstoff By Dr Heinrich Pincass 22 x 15 cm, pp 82 Dresden & Leipzig Verlag von Theodor Steinkopff, 1933 Price RM 6 50, bound RM 7 30

The industrial preparation of cheap hydrogen is one of the outstanding problems of the heavy chemical industry As the lightest gas its cost per ton remains high, although expressed per thousand cubic feet it appears remarkably low A new industry of coal and oil hydrogenation awaits the advent of low priced hydrogen Although there is an extensive literature on the subject, largely scattered in technical publications, there has been hitherto no book summarizing the present state of affairs The present work is commendably short it is primarily written for the chemist

The alternative processes discussed are those starting from water gas, from coke-oven gas, from hydrocarbons, the iron contact process, sundry chemical processes, and the electrolytic, to which last the greatest space is allotted A few pages are devoted to atomic hydrogen and to a list of patent numbers, at the end there is a critical summary and the usual author and subject indices

This is not the place to discuss even the chief points of the various rival processes; the author, like other experts at the present time, leaves the reader to take his choice between water gas and coke-oven gas as the cheapest source of raw material according to the engineering conditions The adoption of the hydrocarbon or electrolytic processes depends on the cost of these gases or of electric energy under specially favourable circumstances Something below 1 shilling per 1,000 cubic feet of hydrogen appears to be the lowest price at which it can be produced even on the largest scale This is a remarkable achievement in relation to the cost of a town's gas at a gas works.

E F Armstrong

STUDIES IN COPRECIPITATION.[1] III

THE WATER CONTENT OF CALCIUM OXALATE MONOHYDRATE

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Calcium oxalate precipitated from aqueous solutions usually consists of the monohydrate. In addition to the one molecule of water of crystallization, the air-dried precipitate contains an excess of water, which may be present (a) in the form of a higher hydrate of calcium oxalate, (b) as occluded water in the interior of the crystal, (c) as adsorbed water at the external and internal surface of the monohydrate (hygroscopic water). In connection with a study of the coprecipitation of various ions with calcium oxalate, it was desirable to have some information on the conditions of formation of the higher hydrates, and their stability, if left in contact with the supernatant liquid. Calcium oxalate monohydrate has been recommended as a weighing form for calcium, the precipitate being weighed in the air-dry state or after heating at 100°C. to 105°C. From the analytical point of view, therefore, it is of great importance to obtain some definite information on the amount of water occluded by the precipitate, and on its hygroscopic character.

THE HIGHER HYDRATES OF CALCIUM OXALATE

The stable form of calcium oxalate is the monohydrate; it forms monoclinic crystals of widely varying appearance. According to G. Hammarsten (2) it is obtained in pure form either by precipitation from concentrated aqueous solutions of calcium salts and oxalate or from much more dilute solutions (0.001 to 0.002 *M*). Hammarsten states that the monohydrate is not hygroscopic in the real meaning of the word, but easily contains nearly 1 per cent of moisture, because of which it must be dried at 30–40°C. This statement is not exact; the pure monohydrate is definitely hygroscopic, as will be shown later in this paper. By precipitation from approximately 0.07 to 0.02 *M* aqueous solutions, a precipitate consisting of a mixture of the mono- and di-hydrate is obtained. At first view it may seem strange that the monohydrate alone is precipitated from more dilute solutions; this behavior, however, may be explained by assuming that at extreme dilutions the solutions are supersaturated only with respect to the monohydrate. According to Hammarsten it is hard to prepare the di-hydrate, which crystallizes in the tetragonal system, in a pure form; it is much easier to isolate the trihydrate, which crystallizes in the rhombic system. Both higher hydrates have been prepared by precipitation from more or less dilute hydrochloric acid solutions. The di- and tri-hydrate are not stable when left in contact with the supernatant liquid and are transformed into the stable monohydrate. Excess of calcium ions inhibits the transformation, whereas oxalate ions favor it. Since in fairly strong acid medium most of the oxalate is present in the form of bioxalate ions and undissociated oxalic acid, it may be expected that free mineral acid will favor the stability of the higher hydrate.

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[1] From a thesis submitted by Ernest B. Sandell (Du Pont Fellow in Chemistry) to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy (1932).

[2] Lack of space prevents the description of precipitations made in acid, alcoholic, etc. solutions. The conditions are merely indicated in table 1. For full details see the thesis of E. B. Sandell, University of Minnesota, 1932.

In the following experiments, calcium oxalate was precipitated under conditions comparable with those obtaining in the study of coprecipitation phenomena. Precipitations were made either by (1) the ordinary method or (2) the method of Hahn (3). In the former case, if calcium was to be in excess during the precipitation, 20 cc. of 0.25 *N* ammonium oxalate were added from a buret to 24 cc. of 0.25 *N* calcium chloride (i.e., an excess of 20 per cent) mixed with sufficient water to give a final volume of 100 cc.; and, conversely, if oxalate was to be in excess, 20 cc. of calcium solution were added to 24 cc. of oxalate. The time of addition of precipitant was one minute. In the method of Hahn, 0.25 *N* calcium chloride and ammonium oxalate solutions were added simultaneously from separate burets to 50 cc. of water at such a rate that one solution was kept 1 cc. in excess of the other throughout the addition; the time of addition was 15 to 20 minutes.[2]

The precipitates were collected by filtration in sintered glass filtering crucibles, washed with alcohol, then with ether, dried by suction in laboratory air and weighed; they were then heated to 100–110°C. to remove water in excess over that of the monohydrate, cooled in a sulfuric acid desiccator, and again weighed; finally the weight was determined after constancy had been reached at room temperature and at the same humidity as before the heating. The difference between the first and third weighings gives the approximate amount of higher hydrate present in the original precipitate. The amount of water present as higher hydrate found in this way is only approximately correct, because it is assumed that the hygroscopic character of the precipitate is not changed by heating to 100–110°C., and that the occluded water is quantitatively taken up again after drying. The figures on the loss of non-hygroscopic water on drying at 100–110°C.,

TABLE 1

Loss of non-hygroscopic water of calcium oxalate precipitates heated at 100°C.

PRECIPITATE NUMBER	MANNER OF PRECIPITATION	LOSS OF NON-HYGROSCOPIC WATER AT 100°C.
		per cent
1a	Oxalate added to excess calcium solution at room temperature	13.7
1b	Oxalate added to excess calcium solution at room temperature	3.7
1c	Oxalate added to excess calcium solution at room temperature	11.4
2a	Precipitated as in 1a, but stood in solution 31 days	0.4
2b	Precipitated as in 1a, but stood in solution 12 days	0.1
2c	Precipitated as in 1a, but stood in solution 20 hours	0.15
3a	Calcium added to excess oxalate solution at room temperature	7.9
3b	Calcium added to excess oxalate solution at room temperature	7.8
4	Precipitated as in 3a, but stood 12 days	0.3
5a	Oxalate added to calcium in hot solution	0.25
5b	Oxalate added to calcium in hot solution	0.3
6a	Calcium added to oxalate in hot solution	0.35
6b	Calcium added to oxalate in hot solution	0.35
6c	As in 6a, except larger excess oxalate	1.0
6d	Precipitated as in 6a, but stood 17 days	0.2
7	Neutralization of cold acid solution containing excess calcium	3.0
8	Neutralization of cold acid solution containing excess oxalate	0.1
9	No. 7 repeated in hot solution	0.2
10	No. 8 repeated in hot solution	0.1
11	Precipitated in dilute HCl solution without neutralization	approx. 15.0
12a	Method of Hahn, cold, calcium in excess	approx. 1
12b	Method of Hahn, cold, calcium in excess	1.2
12c	Method of Hahn, cold, calcium in excess	0.5
12d	As in 12a, but stood 1 month	0.3
13a	Method of Hahn, cold, oxalate in excess	0.6
13b	Method of Hahn, cold, oxalate in excess	0.25
14	Method of Hahn, hot, calcium in excess	0.05
15	Method of Hahn, hot, oxalate in excess	0.1
16	Method of Hahn, cold acid solution, oxalate in excess	0.25
17	No. 16 repeated in hot solution	0.15
18	Method of Hahn, acetic acid solution, room temperature	approx. 6
19	Method of Hahn, alcoholic solution, room temperature	2.0

as reported in table 1, give the amount of water present as higher hydrate of calcium oxalate and part of the occluded water; if these figures are smaller than 0.5 per cent it may be safely assumed that no appreciable amount of higher hydrate was present in the original precipitates. It may be mentioned that the experiments described have not been carried out with the intention of finding the proper conditions of preparing the higher hydrates, but with the view to obtaining the approximate composition of the precipitates prepared under various conditions. Since the higher hydrates are more or less rapidly transformed into the monohydrate when left in contact with the mother liquor, it is difficult to get exactly reproducible results, as the time of filtration and washing differs in the various cases. Especially the precipitates formed at room temperature under ordinary conditions are very finely divided and require several hours to filter and wash.

Transformation of the pure dihydrate into the monohydrate results in a loss in weight of 10.98 per cent; of the trihydrate into the monohydrate of a loss of 19.78 per cent.

DISCUSSION OF RESULTS

1. Calcium oxalate precipitated at room temperature from approximately 0.1 N calcium solution contains more water than corresponds to the dihydrate. A lower water content is found if the oxalate is in excess during the precipitation; this may be explained by the fact that excess oxalate promotes the transformation of the higher hydrates into the monohydrate more than an excess of calcium does. In any case the transformation to the monohydrate is complete if the precipitate is allowed to stand in contact with the mother liquor at room temperature for a day or longer. This transformation takes place much more rapidly at higher temperatures.

2. If the precipitation is made at room temperature from extremely dilute solutions (Hahn's procedure (3)) very little higher hydrate is formed (experiments 12 and 13). Probably the conditions are such that the solution during the precipitation is supersaturated only with respect to the monohydrate. Addition of much acetic acid or alcohol favors the higher hydrate formation in Hahn's method of precipitation, for these substances materially decrease the solubilities of the various forms of calcium oxalate (experiments 18 and 19). Fairly slow precipitation of calcium oxalate from acid solutions at room temperature favors the separation of the monohydrate (solubility effect, experiments 7 and 8).

3. The monohydrate alone is formed under all conditions if the precipitations are carried out in hot solutions.

4. The dry higher hydrates are quickly transformed into the monohydrate on heating at temperatures of 100°C. and above. If kept at room temperature in an atmosphere of relative humidity between 25 and 60 per cent, they slowly lose water and finally are completely transformed into the monohydrate.

WATER OF HYGROSCOPICITY IN CALCIUM OXALATE MONOHYDRATE

Calcium oxalate was precipitated under most varied conditions, collected by filtration in a sintered glass crucible, washed free of electrolytes, and weighed after drying in the air or in a desiccator of constant humidity at room temperature (weight I). The air-dry precipitates were then heated at temperatures of 100–105°, 110°, 115°, 120°, and 125°C., respectively, until constant weight was obtained, then cooled in a sulfuric acid desiccator and weighed in a closed weighing bottle in order to prevent adsorption of water at room temperature (weight II). This precaution was necessary since most precipitates were so hygroscopic that they increased in weight on the balance, if weighed open to the air. The theoretical weight of the calcium oxalate monohydrate was found by one of the following methods.

1. Exactly known amounts of calcium in the form of calcium chloride solutions or of pure calcium carbonate were weighed out, and from this the weight of calcium oxalate was calculated (precipitates 2a, 2b, 8a, 8b, 9, 10, 11, 13, and 14 only).

2. In most cases the calcium content was determined in the precipitates, after they had been dried to constant weight, by converting the oxalate to calcium sulfate and weighing as such. By this procedure any coprecipitated ammonium oxalate or bioxalate was quantitatively removed, whereas all calcium present in the precipitate as calcium hydroxide or chloride was weighed as sulfate. In many cases the oxalate content of the dried precipitates was determined by dissolving a known part in warm dilute sulfuric acid and titrating with permanganate according to the standard procedure, using weight burets instead of ordinary burets, and correcting for the titration error by determining iodometrically the slight excess of permanganate which was required for the color change. These oxalate determinations were accurate to at least 0.1 per cent. As shown by the results in table 2, the ratio of calcium to oxalate is as a rule not exactly equal to 100:100. Sometimes there is a slight excess of oxalate, owing to coprecipitation of ammonium oxalate or bioxalate or oxalic acid; the precipitates obtained from neutral or ammoniacal solutions are usually deficient in oxalate because of coprecipitation of hydroxyl ions in the form of calcium hydroxide. These coprecipitations will be discussed more extensively in following papers. From the above it is evident that the difference between the "theoretical weight" of calcium oxalate and weight II does not give the exact amount of occluded water, even if the latter were entirely removed by drying at 100°C. to 110°C. Nevertheless, these deviations are reported in table 2, since these data are of greater analytical significance than those referring to the exact amount of occluded water.

The water of hygroscopicity was found by exposing the precipitates which had been dried to constant weight at 100–110°C. to air or to an atmosphere of constant humidity (the same as before the heating) until constant weight was obtained (weight III). The difference between weight I and weight II gives the hygroscopic water, which should be the same as that found from weights III and II, in case the adsorption of water is reversible and no higher hydrate is formed. It will be seen that

TABLE 2

Non-essential water of calcium oxalate monohydrate precipitates

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO Ca C_2O_4	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF $CaC_2O_4 \cdot H_2O$				
				Air-dried	Dried at 100–105°C	Dried at 110–115°C	Dried at 115–120°C	Rehydrated
		microns						
1a	0.200 *N* ammonium oxalate added to equivalent amount of 0.200 *N* calcium chloride at 100°C.	<1		+0.90	+0.35 (1)* +0.3 (18)	−0.1 (45)	−0.25 (3) −0.25 (15)	
1b	Same as 1a	<1			+0.45 (18)	+0.3 (18)	−1.4 (22) −1.55 (4) −3.4 (20)	
2a	Excess ammonium oxalate added to 200 cc. of dilute calcium solution at 100°C.			+0.85 *R. H.* = 57 per cent	+0.3 (5) +0.1 (15) +0.1 (15)	−0.15 (18)	−0.55 (22) −7.6 (20)	+0.7 *R. H.* = 57 per cent
2b	Same as 2a			+0.3	−0.2 (12) −0.3 (17)			
3a	20 cc. of calcium chloride added to 24 cc. of ammonium oxalate in 80 cc. of solution at room temperature	<0.5	100.0 100.55	+12.0 (1½) +11.6 (18)	+1.05 (4) +1.1 (18)			2.6 (3d)†
3b	Same as 3a	<0.5		+9.2 (18) +2.05 (3 weeks) *R.H.* = 29 per cent	+0.35 (22)			+1.3 (3d) *R. H.* = 29 per cent
4	3a repeated at 100°C.	1-2	100.0:99.61	+2.2 (2)	−0.20 (48)	−0.35 (1)		+1.79 (24) *R. H.* = 29 per cent

5	50 cc. of 0.25 N calcium chloride added to 50 cc. of 0.50 N ammonium oxalate in a volume of 350 cc. at 100°C.	1	100 0:100 0	+2.2 (3 days)	+0 45 (15)		+0 45 (66)	+1.4 (1 month) *R. H.* = 29 per cent
6	20 cc. of ammonium oxalate added to 24 cc. of calcium chloride in 80 cc. of solution at room temperature	<0 5	100 0:100 76	+16.1 (*R. H.* = 25 per cent +2 05 (3 weeks) *R. H.* = 29 per cent	+0.75 (22)			+1.4 (1 week) *R. H.* = 29 per cent
7	6 repeated at 100°C.	0 5–1	100 0:99 49	+2 15 *R. H.* = 40 per cent	+0 1 (18)			+1 5 (3 months) *R. H.* = 29 per cent
8a	Calcium precipitated from dilute solution very weakly ammoniacal with ammonium oxalate at 100°C.	Coarsely crystalline	100 00:99 00	+0 6 (23) +0 5 (25)	+0 6 (69)		+0 25 (20) −2 6 (45)	
8b	Same as 8a		100 00:99 69				−1 7 (20)	
9	As in 8a except temperature = 25°C.	<1					+0.25 (24)	
10	As in 8a except solution was strongly ammoniacal 20 cc. of 2.5 N ammonia in 200 cc.		100 00:98 34				−3 6 (5) −3 9 (2) −4 5 (3) −9 1 (15)	
11	Similar to 10; 10 cc. of 2 N ammonia in 200 cc. of solution		100 00:99 73	+2 0 +1 5 (66) *R. H.* = 0	+1.15 (2)		+1 05 (40)	
12	Oxalic acid added to calcium solution acidified with HCl; then neutralized at 100°C. with ammonia		100 00:100 09		+0 8 (1) +0 3 (17)		+0 35 (1) +0 2 (1) +0 3 (17)	

TABLE 2—*Continued*

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO $Ca\ C_2O_4$	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF $CaC_2O_4\ H_2O$				
				Air-dried	Dried at 100–105°C	Dried at 110–115°C	Dried at 115–120°C	Rehydrated
		microns						
13	Excess ammonium oxalate added to acid solution of calcium and neutralized at 100°C.	5		+0 85 (20) +0.7 *R. H.* = 0	+0.7 (1)	+0.7 (2)		
14	50 cc. of 0.5 *N* ammonium oxalate added to 50 cc. of 0.25 *N* calcium solution in 300 cc. of hot water + 5 cc. of HCl. Neutralized with ammonia			+1 3 (1½) +0 85 (18) *R. H.* = 0	+0.7 (1) +0 65 (7)		+0.6 (18)	
15	Nearly the same as 14			+1.7 (2)	+0 7 (22) +0.7 (22)		+0.7 (66)	
16	Excess ammonium oxalate added to 50 cc. of calcium solution in volume of 250 cc. 10 cc. of 6 *N* acetic acid present. Temperature = 100°C.			+2 0 (½) +1.05 *R. H.* = 0	+1.05 (1) +1 05 (1)		+1.05 (2)	
17	20 cc. of ammonium oxalate added to 24 cc. of calcium chloride in 80 cc. of solution + 2 cc. of concd. HCl. Temperature = 100°C.			+1 1 (3 days)	+0 2 (20)			+0.95 (4) +1.2 (several weeks) *R. H.* = 57 per cent
18	Same as 17 except 20 cc. of calcium solution added to 24 cc. of diluted oxalate solution			+2.0	+0.9 (20)			+1.9 (4) 2.0 (4) *R. H.* = 60 per cent
19	Excess ammonium oxalate added to 200 cc. of hot dilute calcium solution containing 2 cc. of concd. HCl; then neutralized with dilute ammonia		100 00:100 34	+1.25 (2) +1.05 (2 weeks) *R. H.* = 0	+0 8 (2)	+0.35 (48)		+0.9 (3 weeks) *R. H.* = 29 per cent

20	Method of Hahn. Calcium in excess. Neutral solution. Room temperature	1–2	100 00:99 50	+2.7 (18) +2 6 (24)	+0 7 (2½)	0 5 (20)		+1 9 (44) *R. H.* = 29 per cent
21	Method of Hahn. Oxalate in excess. Room temperature	2–4	100 00:99 95	+3 3 (20) *R. H.* = 40–50 per cent	+1 05 (2½)	+0 85 (20)		+1.3 *R. H.* = 29 per cent
22	Method of Hahn. Calcium in excess. Hot solution	5–10	100 00:99 30	+0 4 (20) *R. H.* = 55 55 per cent	+0 15 (2)	−0 1 (20)		+0 25 (20) *R. H.* = 29 per cent
23	Method of Hahn. Oxalate in excess. Hot solution	ca.5	100 00:99 52	+0 5 (20)	0 0 (2½)	−0 15 (2)		+0 35 (20) *R. H.* = 29 per cent
24	Method of Hahn. Acid solution. Oxalate in excess. Room temperature	2–4	100 00:99 94	+2 3 (24) *R. H.* = 30–40 per cent	+1 05 (18)			+2 2 (100) *R. H.* = 29 per cent
25	Same as 24 except in hot solution.	4		+0 05 (48) *R. H.* = 40 per cent	−0 1 (1) −0 05 (48)			0 0 (100) *R. H.* = 29 per cent
26a	Precipitated in cold neutral solution, then digested at 100°C. for 24 hrs.	3	100 00:99 88	+0 1 (48)	−0 15 (72)			−0 10 (24) *R. H.* = 29 per cent
26b	Same as 26a	3	100 00:99 71	+0 20 (1) *R. H* = 25 per cent	0 00 (2)			+0 2 (24) *R. H.* = 29 per cent
27a	Same as 26a except oxalate in excess	2–3	100 00:99 54	−0 5 (48)	−0 7 (3)			−0 6 (48) *R. H.* = 29 per cent
27b	Same as 27a	2–3	100 00:99 73	+0 11 (1) *R. H.* = 25 per cent	−0 26 (18)			+0 11 (48) *R. H.* = 29 per cent

TABLE 2—*Concluded*

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO Ca C_2O_4	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF $CaC_2O_4\ H_2O$				
				Air-dried	Dried at 100–105°C	Dried at 110–115°C	Dried at 115–120°C	Rehydrated
		microns						
28	Same as 26 except precipitated in hot solution	1–2	100 00:99 58	−0 1 (48)	−0 35 (3)			−0 2 (24) *R. H.* = 29 per cent
29	Same as 27 except precipitated in hot solution	2	100 00:99 73	+0 2 *R. H.* = 30 per cent	−0 05 (3)			+0 1 (48) *R. H.* = 29 per cent
30	Precipitated in neutral solution. Calcium in excess Then digested in presence of dilute HCl for 1 day	3–4	100 00:100 06	+0 05 (24)		−0 05 (48) −0 1 (20)		
31	Same as 30 except oxalate in excess	4	100 00:100 31	−0 2 (24)		−0 25 (48) −0 35 (20)		
32	Precipitation in acetic acid solution followed by digestion	2	100 00:100 2	+0 18 (½) *R. H.* = 30 per cent		−0 10 (1½)		
33	Precipitation in dilute acetic acid solution followed by digestion in ammoniacal solution	2	100 00:100 1	+0 38 (½) *R. H.* = 30 per cent		+0 05 (1½)		
34	Precipitation in acetate buffer, followed by digestion		100 00.100 3	+0 22 (½)	+0 02 (1)			
35	Precipitated as in 34 and digested in ammoniacal solution		100 00:99 8	+0 31 (½)	−0 06 (1)			
36	Precipitation in ammoniacal solution followed by digestion in acetate buffer		100 00:100 1	+0 26 (½)	+0 02 (1)			

* The figures in parentheses refer to the time of drying in hours.

† d = days.

within reasonable limits this water of adsorption can be reversibly removed and taken up. The rehydration takes place fairly rapidly; the weight of the dried precipitates was practically constant after twenty-four hours in most cases. By special experiments it was shown that the hygroscopic character is very strongly pronounced at low humidities; the hygroscopic water content did not materially change at relative water vapor tensions between 25 and 50 per cent.

EXPLANATION OF TABLE 2

In the third column the approximate average crystal size of the precipitate is given; in the fourth, the ratio calcium:oxalate as experimentally determined. The fifth column gives the difference in weight between the air-dried precipitate and the theoretical weight of calcium oxalate monohydrate (the relative humidity (= *R. H.*) of the air in all the experiments was within 25 to 60 per cent and is indicated in the table; *R. H.* = 29 per cent means that the drying was done over deliquescent calcium chloride crystals; *R.H.* = 57 per cent signifies that the drying was done over deliquescent sodium bromide dihydrate at 25°C.). The figures occurring in parenthesis after the percentage deviations refer to the time of drying in hours. The sixth, seventh, and eighth columns give the difference in weight between the dried precipitates and the theoretical. The last column in the table headed "Rehydrated" contains the deviations from the theoretical weights as obtained by exposing the precipitates dried at 100–130°C. to air at relative humidities of 25 to 60 per cent at room temperature and weighing when equilibrium was attained. Such treatment restores most, if not all, of the hygroscopic water lost by heating.

In table 3 the hygroscopic, or reversible, water of the various calcium oxalate precipitates has been given. The data presented in this table have been drawn from table 1 as well as from table 2 as indicated by the numbering of the precipitates. (I refers to table 1, II to table 2). The hygroscopic water was determined by obtaining the weight of the precipitate heated to 105°C., and then placing the precipitate over a saturated solution of calcium chloride hexahydrate or in some other atmosphere of humidity between 25 and 50 per cent, and reweighing after constant weight had been attained. The increase in weight is the amount of hygroscopic water in the precipitate.

In some cases the non-reversible water of the precipitate is also given. The amount of non-reversible water was obtained by weighing the precipitate kept over calcium chloride hexahydrate before and after drying at 105°C. (weight I—weight III). The weight of water not recovered after heating has been called the non-reversible water.

TABLE 3

Hygroscopic water of calcium oxalate monohydrate

PRECIPITATE NUMBER		MANNER OF PRECIPITATION	CRYSTAL SIZE	OXALATE CONTENT	HYGROSCOPIC WATER	NON-REVERSIBLE WATER
			microns	*per cent*	*per cent*	*per cent*
I*	1a	Oxalate added to calcium at R. T.†	<0.5		1.4	
I	1c	Oxalate added to calcium at R. T.	<0.5		0.9	
II‡	6b	Oxalate added to calcium at R. T.	<0.5	100.76	1.0	
I	1b	Oxalate added to calcium at R. T. Stood dry 3 weeks before heating	<0.5		0.5	
II	6a	Same as II b	<0.5		0.65	
I	2c	Oxalate added to calcium at R. T. Stood in solution 20 hours			0.65	<0.15
I	2b	Oxalate added to calcium at R. T. Stood in solution 12 days			0.5	0.1
I	2a	Oxalate added to calcium at R. T. Stood in solution 31 days			0.4	
I	3a	Calcium added to oxalate at R. T.	<0.5		1.7	
II	3a	Calcium added to oxalate at R. T.	<0.5		1.5	
I	3b	Calcium added to oxalate at R. T. Stood dry 3 weeks	<0.5		0.9	
II	3b	Calcium added to oxalate at R. T. Stood dry 3 weeks	<0.5		0.95	
I	4b	Calcium added to oxalate at R. T. Stood in solution 12 days, then dry 5 weeks			0.45	0.15
I	5a	Oxalate added to calcium at 100°C.			1.7	0.2
II	7	Oxalate added to calcium at 100°C.	0.5–1	99.49	1.45	0.6
I	5b	Oxalate added to calcium at 100°C. Stood dry 5 weeks	0.5–1		ca. 0.8	ca. 0.5
I	6a	Calcium added to oxalate at 100°C.			1.8	0.35
II	4	Calcium added to oxalate at 100°C.	1–2	99.61	2.0	<0.4
II	5	Calcium added to oxalate at 100°C. Stood dry 3 days	1	100.0	0.95	0.8
I	6b	Calcium added to oxalate at 100°C. Stood dry 5 weeks			0.7	0.15

I	6c	Similar to I 6a. Stood dry 3 days			0 7	1 0
I	6d	Calcium added to oxalate at 100°C. Stood in solution 17 days and then dry 20 days			0 5	0.2
I	7	Neutralization of acid solution containing excess calcium. R. T.	1–2		1 1	
I	8	Neutralization of acid solution containing excess oxalate. R. T.	1–2		1 05	0.1
I	9	Neutralization of acid solution containing excess calcium at 100°C.			0 7–0 9	0 0
I	10	Neutralization of acid solution containing excess oxalate at 100°C.			1 1	0 1
II	13	Neutralization of acid solution containing excess oxalate at 100°C. Stood dry for several weeks	5		0 15	0 0
II	14	Similar to I 10			0 5	
II	19	Similar to I 10. Stood over sulfuric acid 2 weeks before heating		100 34	0 0 (105°C) 0 5(115°C)	0 35
II	16	Oxalate added to calcium in dilute acetic acid solution at 100°C.			1 0	
II	17	Oxalate added to calcium in dilute HCl solution at 100°C.	Coarse		0 9	0 0
II	18	Calcium added to oxalate in dilute HCl solution at 100°C.	Coarse		1 1	0 0
I	12b	Hahn method. Calcium in excess. R. T.			1.4	
I	12c	Hahn method. Calcium in excess. R. T.			1 2	
II	20	Hahn method. Calcium in excess. R. T.	1–2	99 50	{1 4 1 85 (125°C.)	
I	12d	Hahn method. Calcium in excess. R. T. Stood 1 month			0 6	<0 3
I	13a	Hahn method. Oxalate in excess. R. T.			1 6	
II	21	Hahn method. Oxalate in excess. R. T.	2–4	99 95	1 7	
I	13b	Hahn method. Oxalate in excess. R. T. Stood dry 1 month			0 45	<0 25
I	14	Hahn method. Calcium in excess at 100°C.			0 25	0 05

* I refers to table 1.

† R. T. = room temperature.

‡ II refers to table 2.

TABLE 3—*Concluded*

PRECIPITATE NUMBER	MANNER OF PRECIPITATION	CRYSTAL SIZE	OXALATE CONTENT	HYGROSCOPIC WATER	NON-REVERSIBLE WATER
		microns	*per cent*	*per cent*	*per cent*
II 22	Hahn method. Calcium in excess at 100°C.	5–10	99.30	0.2 0.45 (125°C.)	<0.2
I 15	Hahn method. Oxalate in excess at 100°C.			0.4	0.1
II 23	Hahn method. Oxalate in excess at 100°C.	5	99.52	0.35 0.7 (130°C.)	0.15
I 16	Hahn method. Acid solution. Oxalate in excess. R. T.			1.2	0.05
II 24	Hahn method. Acid solution. Oxalate in excess. R. T.	2–4	99.94	1.15	0.1
I 17	Hahn method. Acid solution. Oxalate in excess. 100°C.	4–5		0.1	0.1
II 25	Hahn method. Acid solution. Oxalate in excess. 100°C.	4		0.1 0.3 (130°C.)	0.05
I 19	Hahn method. Alcoholic solution	<0.5		2.8	
II 26a	Precipitated in neutral solution. Digested. Calcium in excess	3	99.88	0.05 0.45 (130°C.)	0.2
II 26b	Precipitated in neutral solution. Digested. Calcium in excess	3	99.71	0.2 0.1	0.0
II 27a	Precipitated in neutral solution. Digested. Oxalate in excess	2–3	99.54	0.35 (130°C.)	0.1
II 27b	Precipitated in neutral solution. Digested. Oxalate in excess	2–3	99.73	0.35 0.15	0.0
II 28	Precipitated in neutral solution at 100°C. Digested. Calcium in excess	1–2	99.58	0.45 (130°C.)	0.3
II 29	Precipitated in neutral solution at 100°C. Digested. Oxalate in excess	2	99.73	0.55	0.0
II 30	Precipitated in neutral solution at R. T. Calcium in excess. Digested with HCl	3–4	100.06	0.1 (120°C.)	
II 31	Precipitated in neutral solution at R. T. Oxalate in excess. Digested with HCl	4	100.31	0.1	
II 32	Precipitated in acetic acid at R. T. Digested	2	100.2	0.3	
II 33	Precipitated in acetic acid at R. T. Digested in ammoniacal solution	2	100.1	0.3	

DISCUSSION OF RESULTS

1. Calcium oxalate monohydrate, no matter how precipitated, always contains excess water after drying in the air (relative humidity 25 to 60 per cent) at room temperature. On heating to 100°C. and above, part or sometimes all of this is lost, but nearly all is regained if the dried precipitate is allowed to stand in the air. The water lost on heating, therefore, is mostly hygroscopic water. This water can be reversibly taken up and removed. This process, however, is not strictly reversible on account of internal structural changes taking place in the crystalline precipitates on aging (vide infra); but over a short period of time the reversibility of the adsorption of water seems fairly well established.

2. The presence of small amounts of impurities (coprecipitated foreign ions) in the calcium oxalate does not seem to affect the hygroscopicity of the precipitate. Precipitates formed from solutions in which oxalate has been in excess during the precipitation are usually slightly more hygroscopic than those formed in the presence of excess calcium ions. This also proves that the hygroscopicity of calcium oxalate is not primarily due to coprecipitated calcium hydroxide.

3. The monohydrate sometimes decomposes on continued drying at 115–125°C. by losing monohydrate water. The decomposition is generally slow and usually does not begin until the precipitate has been heated for some time. The loss of monohydrate water seems to be limited to precipitates formed in neutral or ammoniacal solutions, especially at 100°C., i.e., to those precipitates which have occluded calcium hydroxide or basic oxalate.

4. Precipitates formed from approximately 0.1 *N* solutions are fairly hygroscopic and contain in the air-dry state 1 to 1.8 per cent of adsorbed water. The hygroscopicity decreases with time of standing (especially at higher temperatures) before filtration, owing to recrystallization of small particles to larger ones and partly to internal perfecting of the crystals, by which process the internal surface is decreased. The distinct decrease of hygroscopicity after digestion in the mother liquor is clearly demonstrated by the results of experiments II 2ba to II 33; the phenomenon is of great analytical significance. Precipitates prepared under the worst analytical conditions, viz., at room temperature from fairly concentrated solutions, and which retain about 1.5 per cent water in the air-dry state if filtered immediately after the precipitation, contain only 0.1 to 0.3 per cent of water of hygroscopicity if digested at 90–100°C. for a day before filtration. *If the precipitation is made at room temperature from about 0.1 N solutions slightly acid* (acetic acid, or acetate buffer, pH 4–6) *and if the precipitate thus obtained is digested in the mother liquor for at least 20 hours at a temperature of approximately 90°C., then a product is obtained which in the air-dry state contains 0.1 to 0.3 per cent of adsorbed water and in*

which the ratio of calcium to oxalate is almost equal to the theoretical (100:100.1 to 100.2) (experiment II 32, 33). In a study of the coprecipitation of foreign ions with calcium oxalate (to be described in following papers), it was found that the purest precipitate is obtained under exactly the same conditions. *Precipitation of calcium oxalate from relatively concentrated solutions at room temperature followed by digestion, therefore seems to be the best procedure from the analytical point of view in spite of the fact that the precipitate is of relatively small size and as a rule cannot be filtered as rapidly as one obtained under ordinary analytical conditions.*

5. A distinct decrease in hygroscopicity is even noticed on the aging of air-dry crystals (experiments I 1b; II 4, 5; I 6b, c, d; I 10; II 13), enough water apparently being present in the interior of the crystals to allow internal structural changes to take place and thus cause a perfection of the crystalline precipitate, by which the porosity of the crystals appears to decrease. From the various examples given in the tables it is evident that a great deal of the adsorbed water is present at the walls of the capillaries in the interior of the crystals. As long as these canals remain in open communication with the exterior, the process of adsorption and desorption will be reversible. If during the process of inner perfection of the crystals the capillaries are all filled by the constituents of the precipitate itself, all the water in the interior of the crystals will be driven out. On the other hand, if dams or similar obstructions are formed in the capillaries, the hygroscopic character will decrease, but the water inside the dams will no longer be in communication with the exterior of the crystal and will remain in the inside as *occluded water;* the latter will be driven out only at high temperatures. From a preliminary study of the internal structural changes taking place in a fresh precipitate, to be described later, it was inferred that the process of "dam-formation" may be quite general, thus explaining why occluded water and coprecipitated foreign ions adsorbed during the growth of the crystals are only partly removed by digesting fairly coarse crystals after precipitation. A more thorough study of the behavior of occluded water under various conditions will be made in the future; calcium oxalate is not a suitable substance for such an investigation, since it already contains one molecule of water of crystallization and under certain conditions forms higher hydrates. The tremendous purification taking place during the digestion of calcium oxalate formed at room temperature from relatively concentrated solutions may be a more or less specific case, since a transformation of the higher hydrates and an entire recrystallization takes place on digestion.

6. Calcium oxalate formed at 100°C. more or less under analytical conditions, is strongly hygroscopic (1 to 1.5 per cent water adsorbed) if collected soon after the precipitation. On aging in contact with the mother liquor, or in the dry state, its hygroscopicity decreases three to four times,

but is higher than that obtained by digesting a precipitate formed in the cold. The phenomenon described under paragraph 5 explains this difference. That the original hygroscopicity is mainly due to the large internal surface is clearly demonstrated by the results of experiments in which the precipitation was made slowly at 100°C. from neutral or weakly acid solutions. The air-dry precipitate still contains about 1 per cent of water of hygroscopicity (I 7, 8, 9; II 16, 17, 18), although fairly coarse particles of calcium oxalate are formed. The same holds for a precipitate prepared at room temperature according to Hahn's procedure (precipitation from extremely dilute solutions). In spite of the fact that the crystal size is of the order of 1 to 4 microns the air-dry crystals still contain 1.5 to 1.8 per cent of water; on aging at room temperature, even in the dry state, the hygroscopic water content decreases three- to four-fold (experiments I 12d, 13a, 13b; II 20). Precipitates obtained according to Hahn's procedure in the presence of 30 to 40 per cent alcohol are strongly hygroscopic (I 19). On the other hand, if the precipitation is carried out at 100°C. according to Hahn, the crystals are only slightly hygroscopic (0.1 to 0.4 per cent of adsorbed water; experiments I 14, 15, 16, 17, 19; II 22, 23, 24, 25).

7. From the figures in table 2 under the heading "Deviation in per cent from calculated weight of calcium oxalate" it is evident that calcium oxalate even after drying at 110°C. is not an ideal weighing form for calcium. High results (indicated by +) must be attributed to occluded water and coprecipitated alkali oxalates or bioxalates, in cases where the ratio calcium : oxalate is smaller than 1.000. Low results may be obtained if there is a hydroxyl coprecipitation (calcium:oxalate larger than 1.000), although a compensation of errors takes place on account of the presence of occluded water.

From the analytical point of view it is gratifying to find that almost theoretical results (within 0.1 per cent) are obtained if calcium oxalate is precipitated at room temperature from not too dilute, weakly acid solutions and digested for twenty hours before filtration. Since such precipitates are virtually free from coprecipitated substances and not very hygroscopic, this procedure seems to be by far the best for the precipitation of calcium oxalate under analytical conditions. The analytical part of this study will be described elsewhere.

SUMMARY

1. Calcium oxalate precipitated at room temperature from approximately 0.1 N calcium solutions contains trihydrate. Oxalate promotes the transformation of the higher hydrates into the monohydrate more than calcium does. In any case this transformation is complete if the precipitate is allowed to stand in contact with the mother liquor at room

temperature for a day or longer, and takes place much more rapidly at higher temperatures. The dry higher hydrates are slowly transformed into the monohydrate at room temperature, if kept at a relative humidity of 25 to 60 per cent. At 100°C. the higher hydrates are quickly transformed into the monohydrate. The monohydrate alone is formed if the precipitations are made in hot solutions.

2. An extensive study has been made of the hygroscopic character of calcium oxalate prepared under various conditions. Calcium oxalate, no matter how precipitated, always contains excess water after drying in the air. The process of adsorption and desorption of water is fairly, but not strictly, reversible on account of internal structural changes taking place in a fresh precipitate on standing.

3. A great deal of the adsorbed water is present at the walls of internal capillaries in the crystals. On aging under the mother liquor, or more slowly in the air-dry state, a decrease in the amount of hygroscopic water is generally noticed. This may be explained by an internal perfection of the crystals on aging, which partly fills up the canals with constituents of the precipitate itself, and mainly by blocking up the canals. In the latter case part of the water remains in the occluded state and is only removed at high temperatures.

4. Calcium oxalate monohydrate, even after drying at 110°C., is not an ideal weighing form for calcium. The purest, and only slightly hygroscopic, calcium oxalate is obtained if the precipitation is made in relatively concentrated solutions, and the mixture is digested for about twenty hours at 90°C. before filtration. During this process a complete transformation of the higher hydrates and an entire recrystallization of the precipitate takes place.

5. Calcium oxalate monohydrate sometimes decomposes on prolonged drying at 115–125°C. with loss of water of hydration. This loss of water of crystallization seems to be limited to precipitates formed in neutral or ammoniacal solutions, especially at 100°C., i.e., to those precipitates which contain occluded calcium hydroxide or basic oxalate.

REFERENCES

(1) Kolthoff, I. M.: J. Phys. Chem. **36**, 860 (1931), for a general discussion of the phenomena of coprecipitation.

Kolthoff, I. M., and Pearson, E. A.: J. Phys. Chem. **36**, 549 (1932), for a discussion of the so-called coprecipitation of zinc with copper sulfide.

(2) Hammarsten, Greta: Compt. rend. trav. lab. Carlsberg **17**, No. 11 (1929), for the extensive study by Hammarsten, in which a literature review and the results of her own studies are given.

(3) Hahn, F. L., and Otto, R.: Z. anorg. allgem. Chem. **126**, 257 (1923).

THE CHEMISTRY OF BERYLLIUM. VI

REACTIONS OF SULFUR DIOXIDE WITH ORGANIC BERYLLIUM COMPOUNDS

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PURPOSES OF THE INVESTIGATION

During studies of electrolysis of beryllium salts in non-aqueous solvents, Booth and Torrey (1) discovered that cold beryllium acetylacetonate rapidly absorbed sulfur dioxide to form a liquid. The sulfur dioxide could be boiled off by gentle warming and recondensed, dissolving the beryllium compound as frequently as desired without any apparent change in the beryllium acetylacetonate. A sample of the sulfur dioxide beryllium acetylacetonate solution containing some crystals was sealed off in a test tube and has remained unchanged for the last eight years.

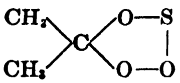
The remarkable absorbing power of this beryllium compound immediately suggested to the discoverers that, in the first place, the study of this reaction might yield information of interest, since it apparently represented a novel type of reaction, possibly a general one, with metallic compounds containing a C:O grouping. The second point is of course the possible application of this reaction to the development of an absorption type refrigerator.

HISTORICAL DISCUSSION

If, as Booth and Torrey thought, the reaction of sulfur dioxide on beryllium acetylacetonate was completely reversible, it would seem probable that the compound formed was of the so-called molecular compound type analogous to hydrates. In other words, the sulfur dioxide was absorbed as sulfur dioxide of crystallization. The question may be raised at once as to whether the absorption of sulfur dioxide is a function of the beryllium or of the organic part of the compound.

A search of the literature reveals no study of the action of sulfur dioxide on beryllium compounds, but certain reactions of sulfur dioxide on organic compounds have been studied.

H. O. Schulze (2) found that acetone absorbed a little less than two moles of sulfur dioxide per mole of acetone at 0°C. Boessneck (3) passed *sulfur dioxide into acetone and found the gas to be absorbed with the evolution of considerable heat. He proposed the formula*

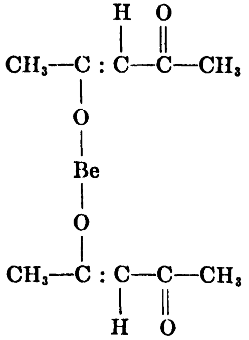


for this liquid compound. On heating it he found that it decomposed into its constituents. Apparently no one has studied this system precisely. Bellucci and Grassi (4) found that sulfur dioxide forms two compounds with camphor (a ketone of higher molecular weight), namely, (1) $SO_2C_{10}H_{16}O$, m.p. −45°C., and (2) $2SO_2.C_{10}H_{16}O$, m.p. −24°C. Very little else has been done with the reactions of sulfur dioxide and ketones.

PLAN OF INVESTIGATION

It was thought that a study of the pressure-concentration relations in this system, at constant temperature, would best establish the nature of the reaction. This study would show: first, the solubility of the compound formed in liquid sulfur dioxide; second, the number of moles of sulfur dioxide reacting with one mole of the compound; third, the vapor pressure of the compound formed; fourth, the vapor pressure of the mixed salt and compound formed.

In order to determine whether it was a function of the beryllium or of other groups in the compound, other beryllium compounds were prepared and tested—such as beryllium basic acetate, beryllium ethyl acetoacetate, etc. Acetylacetone exists as an equilibrium mixture of the enol form and of the keto form, and the beryllium compound is probably



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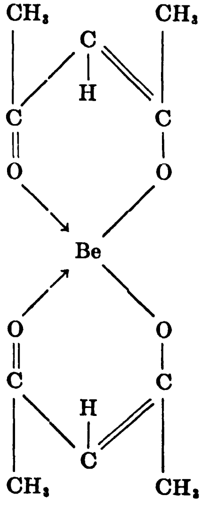


(Sidgwick)

There are two carbonyl groups still free through which the sulfur dioxide may react, or the sulfur dioxide may combine owing to the double bonds.

To see whether other similar enol-keto compounds were reactive with sulfur dioxide, beryllium ethyl acetoacetate and beryllium benzoylacetonate were tried. To check up on the importance of carbonyl groups in the reaction, such a compound as beryllium basic acetate, which contains both beryllium and carbonyl groups, was studied and also certain organic compounds such as benzophenone, urea, acetamide, etc., containing carbonyl groups but no beryllium.

The effect of replacing beryllium by sodium, magnesium, and aluminum, etc., was then tried, as well as a number of other salts of organic acids.

PREPARATION OF COMPOUNDS

The beryllium acetylacetonate, beryllium ethyl acetoacetate, beryllium basic acetate, beryllium benzoylacetonate and sodium acetylacetonate, were prepared in the course of study of the organic salts of beryllium (5). Compounds prepared in a similar manner were magnesium ethyl acetoacetate, magnesium acetylacetonate, and aluminum ethyl acetoacetate. Other compounds were from chemically pure material.

APPARATUS

The apparatus consists of three essential parts: the gas purification system (6), the constant temperature bath, and the baro-buret for measuring gas volumes and pressures (see figure 1). The entire apparatus was constructed of soda-lime glass fused together at all connections.

The constant temperature bath consisted of a gallon capacity Dewar flask, in which was mounted a thermostat (T), lamp for heating, stirrer (S), thermometer, and reaction tube (V). The lamp was controlled by means of a mercury–xylene expansion thermostat through a suitable relay and maintained a constant bath temperature within ±.001°C.

The baro-buret was used because it measures accurately and simultaneously pressure and volume in one instrument and thus cuts down the "dead space" from the buret to the reaction bulb to a minimum (7).

EXPERIMENTAL PROCEDURE

Preliminary tests

Before a system was studied a preliminary test was made in a sample bulb adjacent to the gas supply tank. Here the sample was placed in a suitable reaction bulb of about 5 cc. capacity and sulfur dioxide was condensed on it to see if the sample would dissolve. Slight solubility was checked by evaporating separately the supernatant sulfur dioxide. The preliminary tests showed that at the boiling point of sulfur dioxide, the following compounds were insoluble in sulfur dioxide and *apparently* did not react with it: barium acetate, copper acetate, lead acetate, sodium acetate, sodium formate, ammonium oxalate, ammonium tartrate, aluminum ethyl acetoacetate, magnesium ethyl acetoacetate, sodium acetylacetonate.

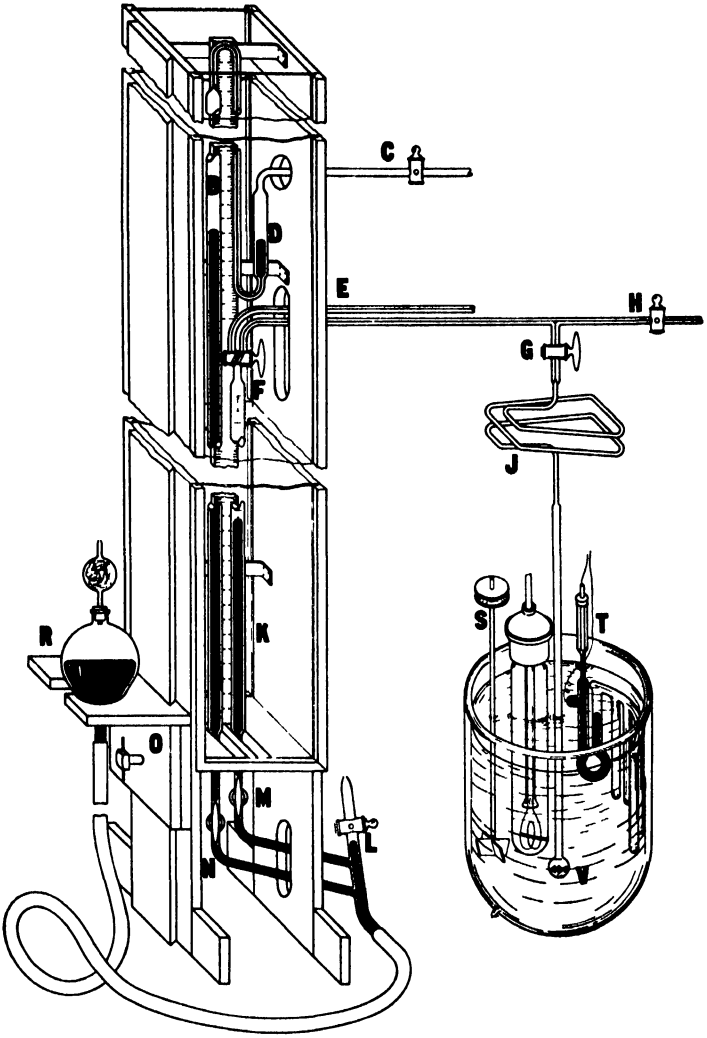


FIG. 1. APPARATUS FOR STUDYING ABSORPTION OF SULFUR DIOXIDE BY ORGANIC BERYLLIUM COMPOUNDS

The following substances seemed to show slight solubility or slight reaction with liquid sulfur dioxide at its boiling point: beryllium benzoylacetonate, magnesium acetylacetonate, benzophenone, urea. The urea seemed to swell in the liquid sulfur dioxide though it did not seem to dissolve.

The following were quite soluble in boiling liquid sulfur dioxide: beryllium acetylacetonate, beryllium basic acetate, beryllium ethyl acetoacetate, acetamide.

Course of a determination

Sulfur dioxide was purified by fractional distillation a sufficient number of times to eliminate all impurities, usually by from eight to twelve distillations. The chief impurities were sulfur trioxide and air. Finally, the remaining gas was solidified with liquid air and the system was evacuated to insure the removal of any residual gas other than sulfur dioxide, and the sulfur dioxide was then boiled into the storage reservoir.

The sample of the compound to be tested was then weighed into the reaction tube (V) (figure 1), which was then sealed into position.

The volume of the reaction bulb (V) connected to the baro-buret was next determined. The system was washed several times with dry, carbon dioxide-free air and the mercury reservoir (R) was lowered, bringing into the buret a sample of the dry carbon dioxide-free air. The stopcock (F) was then turned 180° connecting the baro-buret to the reaction bulb and a number of readings of volume at different pressures were made. From these readings the volume of the reaction tube (V) was calculated by means of the following formula:

$$V = \frac{P_1V_1 - P_2V_2}{P_2 - P_1}$$

The apparatus was evacuated and all but the reaction tube was flushed out with sulfur dioxide several times. A sample of pure sulfur dioxide was then drawn into the baro-buret (K) and its volume and pressure observed and calculated to standard conditions. Connection was then made with the reaction bulb (V) by turning the stopcock 180°, and the pressure was increased by raising the mercury reservoir (R), compelling absorption of the sulfur dioxide. This was continued at increasing pressures until the compound had turned to a liquid or until all the sulfur dioxide was absorbed that would be absorbed at the highest pressure attainable.

If more than one buret full of gas was required the stopcock (F) was turned 180° to draw in a fresh supply of gas from the gas reservoir, the volume and pressure being observed before and after the addition of the fresh quantity. The bath was maintained at 25°C. ± .001°C.

When the reaction had come to equilibrium the pressure, temperature, and volume were read and the total amount of the sulfur dioxide absorbed by the sample was calculated. The mercury reservoir was lowered sufficiently to diminish the pressure in the system about 2 cm.; after standing twenty-four hours to attain equilibrium, the pressure, volume, and temperatures were again observed.

The amount of gas still combined with the sample was calculated by subtracting the total volume passed from the buret from the volume of the gas present in the buret and reaction bulb. This gave the amount of gas freed at each equilibrium, and from this the amount still held was readily calculated.

TABLE 1

The system sulfur dioxide–beryllium acetylacetonate

PRESSURE	MOLES OF SO_2 PER MOLE OF BERYLLIUM ACETYLACETONATE
103 80	1 6600
85 75	1 3680
75 90	1 2090
69 35	1 0990
59 35	0 9620
53 75	0 8650
57 10	0 9110
67 70	0 1310 crystallized
70 40	0 1840
72 25	0 3660
72 65	0 4560
72 85	0 5120
73 05	0 5680
73 40	0 6500
73 65	0 7670
73 65	1 0270
74 40	1 1550
78 50	1 2490
56 40	0 9190
54 95	0 8940
53 55	0 8773
51 20	0 8355
50 45	0 8255
73 70	0 6015 crystallized
62 55	0 0980
53 40	0 0638
41 40	0 0568
16 30	0 0438
7 40	0 0378

This procedure was continued until the pressure reached zero. If the volume of the gas reached the capacity of the buret before the pressure reached zero, the stopcock (F) was turned 180°, exhausting most of the gas in the buret, and then the observations were continued as before.

RESULTS

The data obtained are given in tables 1, 2, and 3, and plotted in figure 2. As the sulfur dioxide was forced into the reaction tube, there was a wetting of the compound on its surface; this became more pronounced as the pressure increased. Finally the entire compound assumed the liquid state, except in the case of beryllium ethyl acetoacetate, which changed first to a gel. As the pressure was reduced the compound remained in liquid state until the solution was considerably supersaturated when suddenly the liquid turned almost explosively to a white solid. This solid was the molecular compound with sulfur dioxide. The compounds could change to liquid under pressure, give up sulfur dioxide, and change to a solid state as many times as desired. In fact they seemed to take up sulfur dioxide more freely after the first pumping.

TABLE 2

The system sulfur dioxide–beryllium ethyl acetoacetate

PRESSURE	MOLES OF SO_2 PER MOLE OF BERYLLIUM ETHYL ACETOACETATE
132 15	1 7820
99 80	1 8000
97 15	1 8300
94 40	1 8580
89 05	1 5570
83 00	1 7260
79 22	1 6020
70 80	1 5470
67 80	1 4290
64 83	1 4630
60 50	1 2990
59 00	0 5676
52 65	0 3590
44 90	0 3100

TABLE 3

The system sulfur dioxide–phenyl benzoate

PRESSURE	MOLES OF SO_2 PER MOLE OF PHENYL BENZOATE
112 85	0 0689
93 40	0 0397

Beryllium acetylacetonate combined with one mole of sulfur dioxide and this compound then dissolved in the sulfur dioxide gas forming a liquid. The portion of the curve (see figure 2) from pressures of 75 cm. to 104 cm. is merely the vapor pressure curve for increasing dilution of this compound dissolved in sulfur dioxide. On cooling, supersaturation is shown in the curve of beryllium acetylacetonate as a dotted line. The beryllium acetylacetonate solution could be supersaturated to the point where approximately only one-half mole of sulfur dioxide per mole of beryllium acetylacetonate was left in the cell. The vapor pressure of the compound $Be(CH_3COCHCOCH_3)_2 \cdot SO_2$ varies between 72 and 76 cm. and averages 73 cm. On carrying the pressure to zero, all the sulfur dioxide was removed and the beryllium acetylacetonate was found to be unchanged.

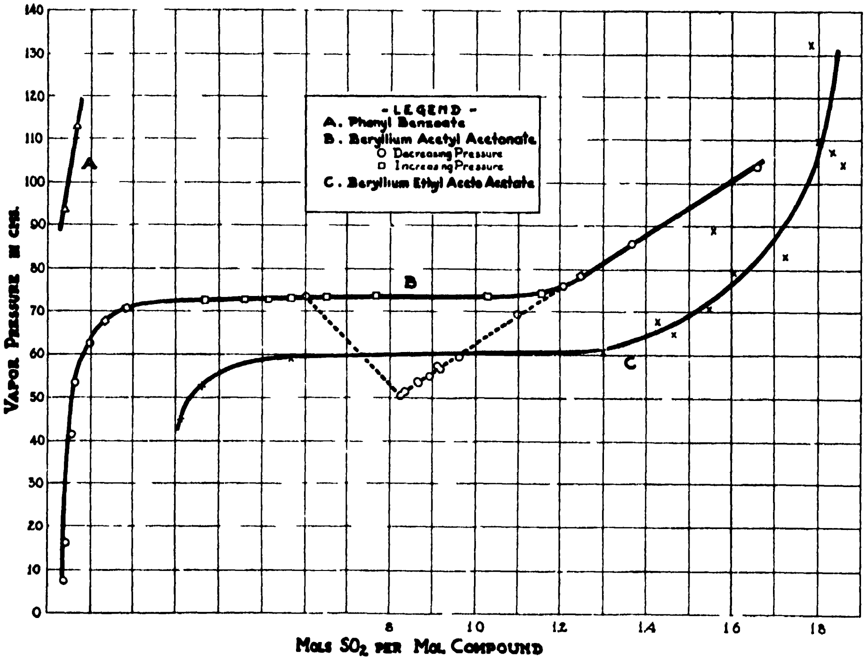


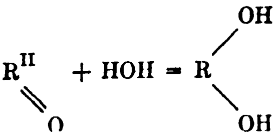
FIG 2 ABSORPTION OF SULFUR DIOXIDE BY ORGANIC BERYLLIUM COMPOUNDS

In the case of beryllium ethyl acetoacetate quite a different condition was found. Instead of combining and forming a true solution, apparently a colloidal solution was formed, since on pumping off the sulfur dioxide during the determination, the liquid first became viscous and then set to a gel. This gel remained quite stable at pressures from 132 cm. down to 60 cm. Finally after pumping off sulfur dioxide at a pressure of 59 cm., the gel suddenly decrepitated leaving a fine powder. The gel formation hindered the free loss of sulfur dioxide and so gave a rather irregular set of points on the upper slope of the curve, although the points are uniformly placed on the horizontal part. The authors restudied this system three times over a period of eight months, without being able to improve the irregularity of these points. This is probably a hysteresis phenomenon (8, 9) due to variation of the capillary pore size as the sulfur dioxide of the gel leaves the solid $Be(CH_3COCHCO\cdot OC_2H_5)_2\cdot SO_2$ structure. This is also suggested by the sudden collapse of the gel on further removal of the sulfur dioxide. The phenomenon may be further complicated by solubility of the compound in the sulfur dioxide. However, the curve shows a general shape similar to the other and the gel reverted to the solid state, showing an approximate composition of 1.0 mole of sulfur dioxide per mole of compound. The vapor pressure of this compound, $Be(CH_3COCHCO\cdot OC_2H_5)_2\cdot SO_2$, averages 80 cm.

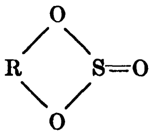
The phenyl benzoate absorbed so little sulfur dioxide that the curve showed plainly that it was merely an adsorption curve; since its further study would contribute nothing it was discontinued.

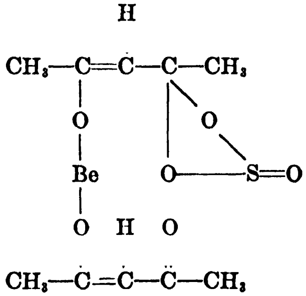
CONCLUSION

It has been established that sulfur dioxide forms addition compounds with beryllium acetylacetonate and beryllium ethyl acetoacetate. In attempting to explain the addition of sulfur dioxide to these compounds several possibilities may be considered. Any rearrangement that is involved must be an easily reversible one; this seems to preclude the possibility of oxidation or reduction. These compounds are apparently of the so-called molecular compound type analogous to the hydrates. Both beryllium acetylacetonate and ethyl acetoacetate formed additive compounds containing one mole of sulfur dioxide to one of the compound. That the addition of sulfur dioxide is not a function of the beryllium alone is suggested by the fact that both Schulze and Boessneck (2, 3) showed that acetone formed an additive compound with sulfur dioxide. However, the organic compounds formed in which sodium and aluminum replace the beryllium apparently do not react with sulfur dioxide– at least below two atmospheres pressure, though the magnesium acetylacetonate shows slight solubility or reaction. These latter compounds are probably more polar than the corresponding beryllium compounds, while the beryllium atom does not change the essentially non-polar character of the original organic compound. The reaction may be analogous to hydration where one of the bonds of the oxygen is opened, permitting the addition of (OH) and (H) thus:



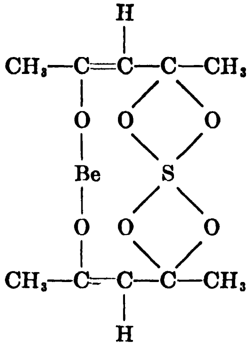
which by analogy in the case of sulfur dioxide would be:





On this basis, however, one wonders why another sulfur dioxide molecule is not taken up by the other =CO group.

An arrangement such as the following in which both =CO groups are involved is unorthodox, since it produces a twelve-membered ring of which other examples are practically unknown; furthermore the sulfur dioxide compound should be more stable if this were its structure:



The fact that only beryllium chelate compounds, beryllium acetylacetonate, beryllium ethyl acetoacetate, and beryllium basic acetate react with sulfur dioxide readily would suggest that the reaction took place via the atom of beryllium were it not for the fact that magnesium acetylacetonate also reacts to a certain extent, and that acetone itself reacts readily.

It will be remembered that liquid sulfur dioxide is an excellent solvent for non-polar compounds in general, particularly esters and fats, in which of course there is a =CO group. It may be that the character of the beryllium in these chelate compounds is sufficiently negative so that they behave towards sulfur dioxide exactly like such non-polar compounds as the fats, which contain no metals. In a former paper (10) it was reported that the hydrolysis of beryllium basic acetate was very slow and difficult, indicating extremely slight ionization to yield Be^{++} ions and that the beryllium was acting in a rôle not unlike that of carbon itself.

The evidence seems to point to the formation here of molecular compounds as a function of the carbonyl group of compounds in which the metal present does not diminish the non-polar character of the organic compound. It would be interesting to test boron chelate compounds with sulfur dioxide if they could be prepared. They should react in a similar fashion, though this would be complicated by the known characteristic of boron compounds to form molecular compounds.

SUMMARY

1. The systems sulfur dioxide–beryllium acetylacetonate and sulfur dioxide–beryllium ethyl acetoacetate have been studied at 25°C. It is found that these beryllium compounds combine in the ratio of one mole of compound to one mole of sulfur dioxide.

2. The vapor pressure of the compound $Be(CH_3COCHCOCH_3)_2 \cdot SO_2$ averages 73 cm. and that of the compound $Be(CH_3COCHCO \cdot OC_2H_5)_2 \cdot SO_2$ averages 60 cm.

3. The nature of these compounds and their possible structure is discussed.

4. The baro-buret is found to be a valuable tool in studying gas-solid equilibria.

REFERENCES

(1) Booth, H. S., and Torrey, G. G.: J. Phys. Chem. **35**, 2476 (1931).
(2) Schulze, H. O.: J. prakt. Chem. [2] **24**, 168 (1881).
(3) Boessneck: Ber. **21**, 1906 (1888).
(4) Bellucci and Grassi: Atti accad. Lincei **22**, II, 675–80 (1913).
(5) Booth, H. S., and Pierce, D. G.: J. Phys. Chem. **37**, 59–78 (1933).
(6) For description of operation see J. Chem. Education **7**, 1249 (1930).
(7) Booth, H. S.: Ind. Eng. Chem., Anal. Ed. **2**, 182–6 (1930).
Booth and Jones: Ibid. **2**, 237 (1930).
Booth and Willson: Ibid. **4**, 427 (1932).
(8) Van Bemmeln: Die Absorption, pp. 196, 214, 232 (1910).
(9) Van Bemmeln and Anderson: Z. physik. Chem. **88**, 191 (1914).
(10) Booth, H. S., and Torrey, G. G.· J. Phys. Chem. **35**, 2468 (1931).

SOME ERRORS INHERENT IN THE USUAL DETERMINATION OF THE BINARY FREEZING POINT DIAGRAM

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It has long been known that there are marked abnormalities in the freezing points of many binary mixtures near the eutectic composition, but it has never been shown definitely whether they are inherent in the system or whether they are merely apparent abnormalities due to experimental error. If, however, one were to study by the usual approximate method a nearly ideal system for which the accurate data are available, a comparison of the corresponding freezing point-composition diagrams should disclose some interesting facts, since all the differences would be due to experimental error.

Most of the temperature-composition diagrams in the literature have been constructed by the use of the Beckmann method, which consists essentially in cooling the melt below the freezing point, inoculating with the proper kind of crystal, stirring, and noting the maximum temperature to which the thermometer rises. The freezing points so obtained are usually low, owing mainly to two causes: (1) the change in the composition of the liquid due to the solid frozen out, and (2) the thermometer lag.[2] The errors thus involved increase as the eutectic is approached. In many cases the eutectic point itself is not experimentally determined but is obtained by extrapolation of the two branches of the curve.

This investigation had for its purpose the study of the nature and the possible magnitudes of the effects due to such inaccuracies on the freezing point-composition diagram, the calculated heats of solution, and on the conclusions drawn as to the ideality of the system. The system β-chlorocrotonic acid–β-chloroisocrotonic acid, for which the accurate freezing point and heat content data have recently been published (1), affords an excellent opportunity for a study of this kind. The results obtained show that the eutectic composition as well as the eutectic temperature is affected by the usual inaccuracies of the data. Other causes of error near the eutectic point are pointed out by means of cooling curves.

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[2] This error may undoubtedly be quite considerable and the fact that in the system here studied it was eliminated, partially counterbalances the fact that our other error was deliberately enhanced. Another cause of low freezing point results is the use of too little undercooling. Since this has been repeatedly discussed (see, for example, Ostwald-Luther, Hand- und Hilfsbuch zur Ausführung physikochemischer Messungen, Leipzig, 1925) and has been eliminated in this work, it will not be considered here.

EXPERIMENTAL

The freezing point method used was one which exaggerated the error due to the separation of the solid, but which practically eliminated the error due to the lag in the thermometer registration.

Apparatus

The apparatus used was the inner part of the cooling curve apparatus previously described (1). It consisted essentially of a small thin-walled glass tube, 6 mm. in diameter, containing the sample (0.7 to 1.0 gram) into which a thermoelement, protected by a thin-walled capillary glass sheath, was inserted through a stopper. This stopper was provided with another small opening through which the undercooled melt could be inoculated by introducing the proper crystals on the end of a glass thread. The thermoelement used was the same as that used in the accurate construction of the diagram for this system.

Procedure

The freezing point determinations for this system were made as follows. A known weight of the component A was placed in the freezing point tube and a small amount of component B was then weighed in by difference without removing the thermoelement. After the mixture was made homogeneous by melting completely and stirring, the freezing point was found by allowing the system to cool in the air (without any shield), seeding at the proper time, stirring, and noting the maximum to which the temperature rose. This was repeated with various degrees of undercooling and the highest maximum obtained was taken as the freezing point for that composition. A little more of substance B was then weighed into the tube and a new determination made. The error in composition is thus cumulative but is estimated to have been at all times less than 0.3 per cent.

Materials

The synthesis and purification of the two acids has been described (1).

The experimental results

The data obtained by the present method are given in table 1. N is the mole fraction in the liquid of the form crystallizing at the freezing point, t°C., T°K; t' is the true freezing point obtained by interpolation of the experimentally correct[3] data for the system. These data are plotted in figures 1 and 2.

The following facts should be noted:

From the temperature-composition diagram, figure 1, it is obvious that the values obtained by the rough method are all lower than those accurately determined. Further, it is apparent that the deviations become increasingly greater as the eutectic is approached and that the eutectic point is shifted by these inaccuracies not only along the temperature axis but also along the composition axis, the extrapolated temperature being about 38.9°C. instead of 41.5°C., and the per cent of β-chlorocrotonic acid being about 33.2 instead of 30.8.

TABLE 1

Experimental freezing point data for the system β-chlorocrotonic acid–β-chloroisocrotonic acid

N	$1 + \log N$	t	$\frac{1000}{T}$	t'	$t' - t$
		β-chlorocrotonic acid branch			
1 000	1 0000	93 6	2 727	93 6	0 0
0 475	0 6767	55 5	3 043	59 1	3 6
0 434	0 6375	52 4	3 072	55 4	3 0
0 389	0 5900	47 0	3 124	50 9	3 9
0 350[a]	0 5440	41 1	3 183	46 8	5 7
		β-chloroisocrotonic acid branch			
1 0000	1 0000	60 5	2 998	60 5	0 0
0 9555	0 9802	57 8	3 022	57 9	0 1
0 9271	0 9671	56 0	3 038	56 3	0 3
0 9077	0 9579	54 8	3 049	55 2	0 4
0 889	0 9489	53 9	3 058	54 2	0 3
0 840	0 9243	50 7	3 088	51 3	0 6
0 810	0 9085	48 5	3 109	49 5	1 0
0 788	0 8965	46 9	3 125	48 1	1 2
0 750	0 8751	44 1	3 153	45 7	1 6
0 725	0 8603	42 3	3 171	44 1	1 8
0 706	0 8488	41 3	3 181	42 8	1 5

[a] Eutectic point by extrapolation = 38 9°C.

From the plot of $(1 + \log N)$ against $\frac{1000}{T}$, figure 2, it is seen that a straight line may be drawn through the inaccurate data in such a way that the greatest deviation corresponds to only about 0.5°C. The heats of solution calculated from the slopes of these lines by means of the ideal freezing point-solubility equation are 4970 and 3940, as compared with the values 5220 and 4120 calories per mole calculated from the accurate lines for the β-chlorocrotonic and the β-chloroisocrotonic acid respectively. It is further apparent that the points near the eutectic show a tendency to fall off gradually, especially on the β-chlorocrotonic acid branch where the eutectic composition is considerably removed from the pure substance. If curved lines be drawn through the points and the heats of solution calculated from their initial slopes, the error would obviously be lessened.

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[3] With a maximum error of 0.25°C. near the eutectic point.

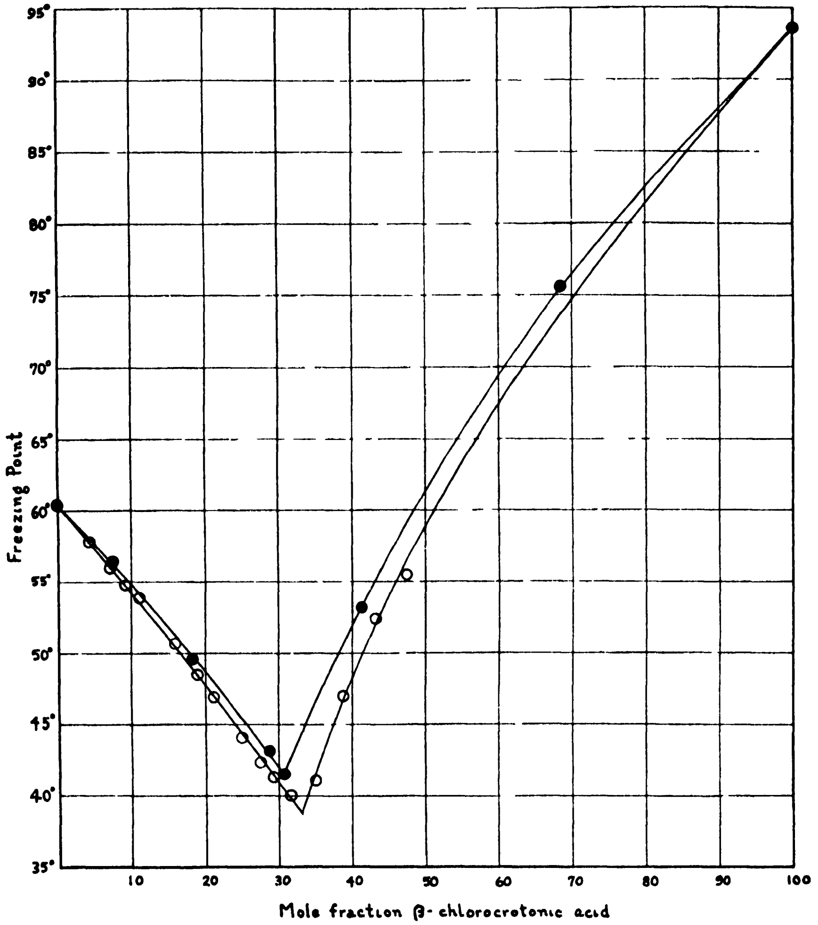

FIG. 1. FREEZING POINT-COMPOSITION DIAGRAM OF THE SYSTEM, β-CHLOROCROTONIC ACID–β-CHLOROISOCROTONIC ACID

Dots represent accurate freezing points; circles represent rough freezing points

DISCUSSION

There are several possible reasons for the increased deviations near the eutectic point which should be pointed out since, to the best of our knowledge, this situation has never been carefully analyzed.

(1) It can be shown that for purely mathematical reasons the error in the mole fraction caused by the freezing of a given fraction of a component of a binary solution increases with the mole fraction of the added component until the two mole fractions are about equal. Let n_A and n_B be the number of moles of A and B respectively in a binary solution and let a be the number of moles and $x = a/n_A$, the fraction of A crystal-

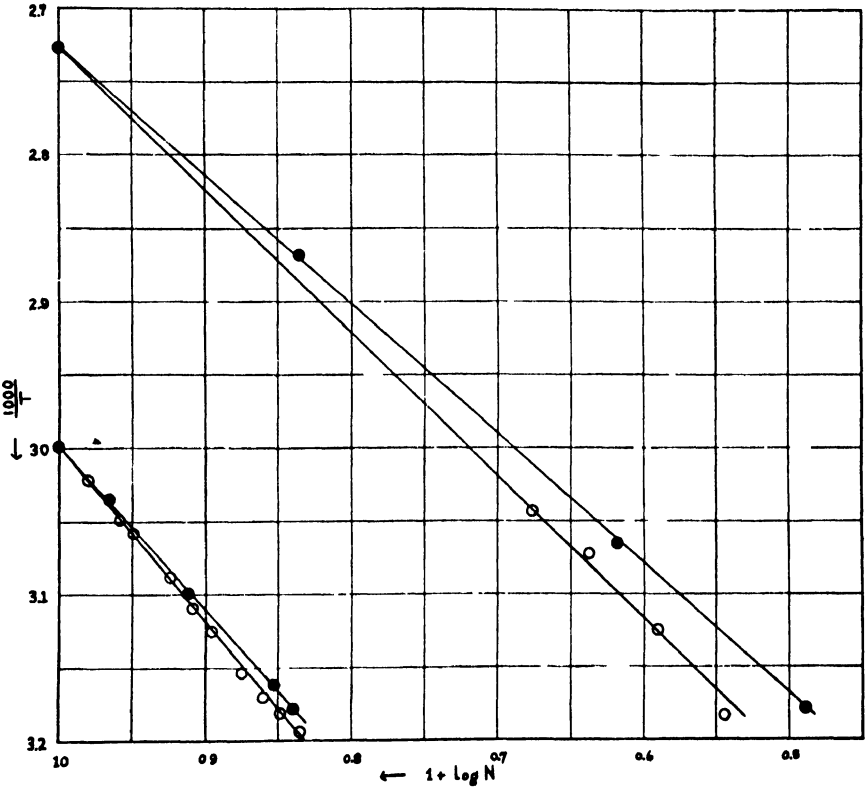

Fig. 2. Log $N - \frac{1000}{T}$ Plot for the System, β-Chlorocrotonic Acid–β-Chloroisocrotonic Acid

Dots represent values calculated from accurate freezing points; circles represent values calculated from rough freezing points. Upper curves are for β-chlorocrotonic acid; lower curves are for β-chloroisocrotonic acid.

lized from this solution in a freezing point determination. Let N_A and N_B be the mole fractions of A and B, respectively, in solution before crystallization and N'_A and N'_B be the corresponding quantities after a moles of A have been crystallized. Then

$$\Delta N_A = N'_A - N_A = \frac{-aN_B}{n_A + n_B - a} = \frac{-xN_AN_B}{1 - xN_A} \doteq -xN_AN_B \tag{1}$$

Differentiating, we obtain

$$\left[\frac{\partial(-\Delta N_A)}{\partial N_B}\right]_x = \frac{x(N_A - N_B - xN_A^2)}{(1 - xN_A)^2} \doteq x(N_A - N_B) \tag{2}$$

From the approximate derivative the change in composition reaches a maximum when $N_A = N_B$. From the accurate derivative the maximum is reached when $N_A = \frac{1 - \sqrt{1 - x}}{x}$. Thus when $x = 0.01$ the maximum occurs at $N_B = 0.4987$.[4]

(2) The general shape of the freezing point-composition diagram adds another source of error. Suppose the error mentioned in (1) be made uniform and small by keeping ΔN_A constant throughout the range of concentration, that is, by decreasing the value of x as we approach the eutectic so as to satisfy equation 1. The error would still usually increase owing to the fact that the change in freezing point for a given change in composition also commonly increases as the eutectic point is approached. This is obvious from the fact that the freezing point-composition lines are ordinarily curved downward. For the ideal solution at constant pressure this follows from the well-known equation,

$$s = \frac{dT}{dN_A} = \frac{RT}{N_A\,\Delta S_A} = \frac{RT^2}{N_A\,\Delta H_A} \tag{3}$$

where, at temperature T, N_A is the mole fraction in solution, ΔS_A is the molal entropy of fusion, ΔH_A the molal heat of fusion of the component crystallizing, and s is the slope of the freezing point-solubility curve. Differentiating we obtain,

$$\frac{ds}{dT} = -\frac{1}{N_A\Delta S_A}\left[2R - \Delta S_A - \frac{R\Delta Cp_A}{\Delta S_A}\right] = \frac{T}{N_A\Delta H_A}\left[2R - \frac{\Delta H_A}{T} - \frac{RT\Delta Cp_A}{\Delta H_A}\right] \tag{4}$$

where ΔCp_A is the molal increase in heat capacity of pure A on fusion. Hence whenever $2R < \frac{\Delta H_A}{T} + \frac{RT\Delta Cp_A}{\Delta H_A}$, s increases with fall in temperature. This is the usual case. If ΔH_A is independent of T then the slope must increase as T decreases whenever[5]

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[4] It is thus obviously true that for a certain definite *amount* of component A crystallizing from a solution, the error in composition so caused increases as the eutectic point is approached.

$$2R < \frac{\Delta H_A}{T}$$

It also follows that the slope changes with temperature in the converse manner whenever ΔS_A is less than $2R$, 3.97 calories or 16.63 joules per degree per mole, and will remain constant if $\Delta S_A = 2R$ entropy units per mole. Thus the solubility in an ideal binary system may start with a positive value of s, pass through an inflection point and approach the eutectic point with a negative value of s. This may even happen when ΔH_A is independent of T and ΔCp_A is zero, for although ΔS_A is then independent of T alone it is a function of N_A which decreases with temperature and consequently ΔS_A actually increases as T decreases. This follows from the relation, valid at constant pressure,

$$\mathrm{d}\Delta S = \frac{\Delta Cp}{T} \mathrm{d}T - R\mathrm{d} \ln N$$

It also follows directly from the definitional relation between ΔS_A, ΔH_A and T_A. Values of the increase in s with falling temperature calculated by means of equation 4 agree satisfactorily with those determined by us for the system composed of the two β-chlorocrotonic acids.

For most of the substances for which apparently reliable direct calorimetric data are given, and especially for organic compounds, the molal entropies of fusion at the freezing points exceed $2R$. The comparatively few exceptions which we have noticed are hydrogen bromide (one crystalline form), hydrogen chloride, hydrogen iodide, pyrosulfuric acid, nitric acid, silver bromide, strontium chloride, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, carbon tetrachloride, methane, methanol, cyclohexane, cyclohexanol, and 1,4-dihydronaphthalene. The elements comprise the largest list of exceptions. Indeed, all the elements for which we have data have entropies of fusion at their melting points which are less than $2R$ per formula weight, except chlorine, bromine, bismuth, gallium, and antimony.

There are a few substantially ideal[6] binary systems in which one compo-

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[5] This relation for the special case where ΔH_A is constant has been developed in a somewhat different manner by van Laar (Proc. Acad. Sci. Amsterdam **5**, II, 424 (1903)).

[6] The criterion of ideality used is that

$$\Delta H_A = -2.303\, R \frac{\mathrm{d} \log N_A}{\mathrm{d}\ (1/T)}$$

where ΔH is the calorimetrically measured molal heat of fusion of component A, the solvent. Strictly, this heat of fusion should be taken at temperature T, but in many cases it can only be evaluated at the melting point.

nent is one of the substances listed above. These systems bear out, at least qualitatively, the relations demanded by equation 4. For example, from the heat data of Latimer (2), the slope of the T—N curve for carbon tetrachloride should decrease with falling temperature until the transition temperature is reached and then increase. Judging from the data of Biltz and Meinecke (3), this is exactly what happens when chlorine is the solute. The same condition should exist for cyclohexane (4) and is actually realized in the binary system with methyl cyclohexane (5).

The combined effect of the above two sources of error upon the observed freezing point of an ideal binary solution can be calculated from equation 3 integrated assuming ΔH_{A} to be independent of T. Then, in general,

$$T = \frac{T_{\mathrm{A}} \Delta H_{\mathrm{A}}}{\Delta H_{\mathrm{A}} - RT_{\mathrm{A}} \ln N_{\mathrm{A}}} \tag{5}$$

and

$$-\Delta T = T - T' = \frac{RT_{\mathrm{A}}^2 \, \Delta H_{\mathrm{A}}}{(\Delta H_{\mathrm{A}} - RT_{\mathrm{A}} \ln N_{\mathrm{A}})\,(\Delta H_{\mathrm{A}} - RT_{\mathrm{A}} \ln N'_{\mathrm{A}})} \ln \frac{N_{\mathrm{A}}}{N'_{\mathrm{A}}} \tag{6}$$

in which T_{A} is the freezing point of pure A; T is the true, T' the observed freezing point of the solution; $-\Delta T$ is the lowering of the freezing point of the solution caused by the crystallization of some of component A; the other terms have the same significance as before. Since N'_{A} would be nearly equal to N_{A} in any properly conducted experiment,

$$\ln \frac{N_{\mathrm{A}}}{N'_{\mathrm{A}}} \doteq \frac{N_{\mathrm{A}}}{N'_{\mathrm{A}}} - 1$$

hence,

$$-\Delta T \doteq \frac{RT_{\mathrm{A}}^2 \, \Delta H_{\mathrm{A}}}{(\Delta H_{\mathrm{A}} - RT_{\mathrm{A}} \ln N_{\mathrm{A}})^2} \, \frac{x}{1 - x} \, N_{\mathrm{B}} \tag{7}$$

Thus for an ideal solution of a given composition the error in freezing point due to crystallization is directly proportional to x provided this is small compared to unity.

Upon differentiating equation 7 we obtain,

$$\left[\frac{\partial(-\Delta T)}{\partial N_{\mathrm{B}}}\right]_x = \frac{R^2 T_{\mathrm{A}}^3 \, \Delta H_{\mathrm{A}}}{(\Delta H_{\mathrm{A}} - RT_{\mathrm{A}} \ln N_{\mathrm{A}})^3} \, \frac{x}{1 - x} \left[\frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}} - \ln N_{\mathrm{A}} - \frac{2N_{\mathrm{B}}}{N_{\mathrm{A}}}\right] \tag{8}$$

Whether the error in T increases, remains constant, or decreases with N_{B} is then determined by whether

$$\frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}} - \ln N_{\mathrm{A}} \gtreqless \frac{2\mathrm{N}_{\mathrm{B}}}{\mathrm{N}_{\mathrm{A}}}$$

Thus the entropy of fusion at the freezing point and the mole fraction are the determining factors. The entropy of fusion of many organic compounds is about 13 calories per degree per mole (6). A substance with this entropy of fusion will show an increase in $(-\Delta T)$ with N_B until the latter reaches 0.8; while if its entropy of fusion is as low as 2.6 it will show an increase in $(-\Delta T)$ up to $N_B = 0.5$. Hence, if the eutectic composition is not too near that of either pure component (B in this case) it is fair to assume that as component B is continuously added to a fixed amount of A and the amount of A crystallized is kept constant the error in the freezing point will usually continuously increase until the eutectic is reached. This would also be the case for varying amounts of A if the fraction removed each time were kept constant. For example, in the case of β-chlorocrotonic acid, whose entropy of fusion is 13.5 calories per degree per mole at its freezing point, if one per cent be crystallized during a freezing point determination the error in T would be 0.05°C. when its mole fraction is 0.9. This error would increase continuously and become 0.27°C. when its mole fraction is 0.308. This is the composition of the eutectic with β-chloroisocrotonic acid.

In order to maintain a constant error in T along a single branch of the curve, x should be decreased as N_B increases in accordance with equation 7. Again using β-chlorocrotonic acid as an example, we find that for a value of $(-\Delta T) = 0.1$°C. we may crystallize 1.9 per cent of the acid when $N_B = 0.1$, but only 0.37 per cent at the eutectic with its isomer when $N_B = 0.692$. Thus x must be decreased fivefold. Since the molal heat capacities of these two isomers in the liquid state are nearly equal (1), it follows that x is practically proportional to the amount of undercooling; hence the latter should be decreased about fivefold in going from $N_B = 0.1$ to the eutectic.

(3) A third error is introduced by the fact that a actually *increases* as the eutectic is approached, owing to the decrease in the rate of crystallization with the decrease in temperature and the attendant increase in viscosity. That slow crystallization in general causes a larger amount of solid to separate before the maximum is reached can perhaps be shown best by a comparison of cooling curves. In figure 3 the line ABC′D′ represents a typical time-temperature curve for a slow crystallization and the line ABCD, a curve for a more rapid one. GH represents the course taken by the temperature of the shield or surroundings. The shaded area in each case, horizontally and diagonally respectively, is proportional to the amount of solid separated at the maximum temperature (7). It is obvious that the area A′BC′F′E′ is greater than the area ABCFE. It was actually found on reëxamining the cooling curves obtained in the earlier study of this system (1) that those for the nearly pure substances were of the rapid type whereas those for compositions near the eutectic were of the slow type.

All of the errors so far considered have been due to failure to correct for the change in composition when the solid separates and they are involved in the case of all solutions, being usually greatest at the eutectic and decreasing as the pure substance is approached. Another source of very considerable error, which may or may not be quite general to all systems, is illustrated by a number of cooling curves obtained for compositions near the eutectic. In these curves the first maximum after inoculating was actually below the true eutectic temperature and after the usual fall in temperature there followed another rise, this time to a higher maximum corresponding to the eutectic temperature. In one case the primary freezing point, after roughly correcting for the amount of solid separated, was 0.5°C. below the eutectic temperature which in this case is actually about 0.5°C. low. This curve, for the composition 31.2 per cent β-chlorocrotonic acid, is reproduced schematically in figure 4 and the cause of the behavior can be explained by a consideration of figure 5 in which the effect is shown much exaggerated.

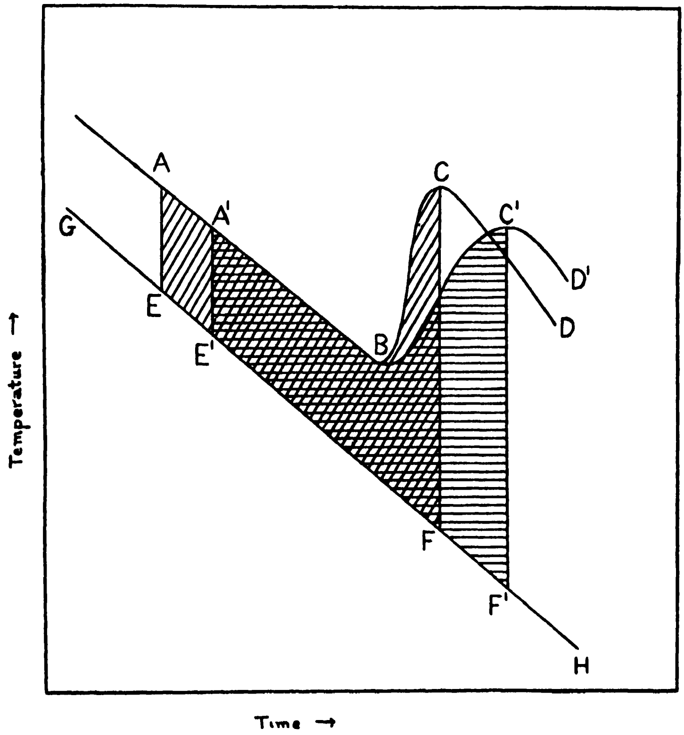

Fig 3 Typical Cooling Curves for Rapidly and Slowly Crystallizing Binary Mixtures

Let us consider that AEB (figure 5) is the correct freezing point-composition diagram for a system as obtained by an accurate method. Owing to the tendency to undercool, a melt of the composition X fails to crystallize, when inoculated with both kinds of crystals, until the temperature is *below* F. The component A then crystallizes giving a primary freezing point corresponding to F (when corrected for the pure A which has separated) and after the maximum is reached, A continues to separate changing the composition of the liquid as it cools, along the line FG until B begins to crystallize.[7] The composition and temperature then change to the eutectic point.[8]

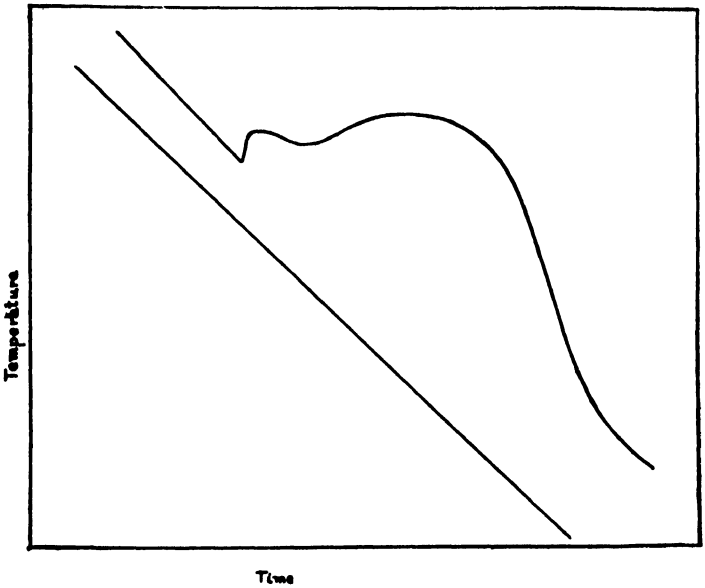

FIG. 4 TYPICAL COOLING CURVE SHOWING PRIMARY FREEZING POINT BELOW THE EUTECTIC TEMPERATURE

For the true eutectic composition the first maximum should on this basis fall below the eutectic flat, but the freezing point obtained by the proper correction for the solid separated should be the true eutectic temperature.

[7] It will be noted that below the eutectic the increase in the degree of undercooling with respect to B is the resultant of two superimposed effects: (a) the lowering of the temperature of the liquid, and (b) the increase of the true freezing point of the liquid due to the continual change toward a composition richer in B.

[8] The true eutectic temperature may never be reached, however, owing to a low rate of crystallization of B, or owing to the fact that the amount of liquid left is so small that its heat of crystallization is insufficient to raise the temperature of the whole sample through the required range. Thus, as mentioned above, the second maximum in figure 4, though higher than the first, is still about 0.5°C. below the true eutectic temperature.

In fact, one would expect that compositions even a little richer in A would show this same characteristic. Cooling curves of this type were actually realized; for example, the sample containing 30.0 per cent of β-chlorocrotonic acid upon inoculation at 38.5°C. came to a maximum of 41.5°C., and then dropped to 39.9°C., and finally rose again to 41.5°C., the eutectic temperature.[9] For compositions richer than the eutectic in component B, the degree of undercooling necessary in order to reach curve AG increases and eventually attains such a value that B is the first to crystallize upon inoculation. The resulting effect on the temperature-composition diagram

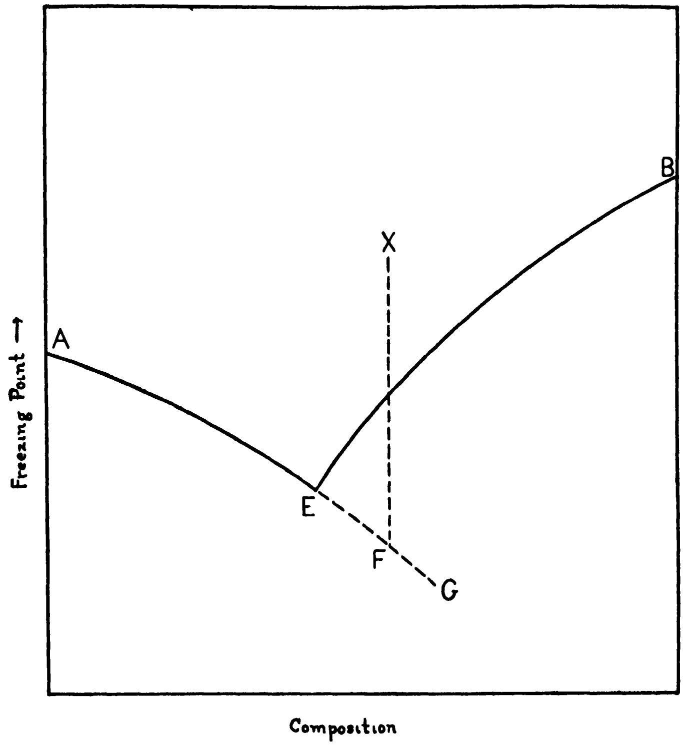

FIG. 5. SCHEMATIC BINARY FREEZING POINT DIAGRAM WITH ONE BRANCH EXTENDED BELOW THE EUTECTIC

would be the extension of the A branch beyond the true eutectic and the distortion of the other branch to meet it.

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[9] It is no novel observation that a system can be undercooled below its eutectic point. Indeed, it is claimed that this can usually be done intentionally whenever one, or both, of the components is capable of being undercooled when pure. To the best of our knowledge, however, no cooling curve like our figure 4, with two maxima, the second higher than the first, has been reported. Such a curve affords the first experimental proof of the validity of the explanation usually given for the cause of such abnormal freezing points.

It is probable that in many systems the cooling of the liquid below the eutectic temperature can occur only to a very limited extent. In such cases the effect on the diagram would be such as to indicate compound formation; that is, a horizontal line would extend between the two branches of the diagram at or just below the eutectic temperature. A case of this kind has actually been pointed out by Bell and McEwen (8), who upon reconstructing the diagram for the binary system of *m*-nitrotoluene with *p*-nitrotoluene found it to be a system of the simple eutectic type instead of one showing compound formation as had been reported previously by Gibson, Duckham, and Fairbairn (9).

CONCLUSIONS

When it is considered that the usual method employed for freezing point determinations involves merely the determination of the height of the first maximum after inoculation and that there is no correction for the solid separated, it becomes obvious that the construction of the freezing point diagrams of many of the binary systems in the literature may be considerably in error. This is particularly in evidence near the eutectic point and may lower the apparent eutectic temperature; in fact, as shown by the discussion of figure 4, this danger exists even if correction is made for the separation of the solid. A shift in the eutectic composition is also to be expected where the temperature deviation on the two branches of the curve is not the same at the true eutectic composition. It should be noted, however, that whereas all the errors discussed in this paper conspire to make the apparent eutectic temperature too low, they may conceivably have opposing effects on the shift of the eutectic composition. Such would have been the case, for example, if the branch BE instead of AE in figure 5 were the one that could be extended. If the extension of neither of these branches were realizable, the diagram obtained might conceivably lead one to believe that there was compound formation. This is obvious from inspection of figure 1.

Erroneous data would, in general, be expected to give a $\log N - \frac{1}{T}$ plot with a curvature which is too great, and the heat of solution calculated from its slope would be too low and would vary more over the temperature range in question than the true heat of solution.

Little can be said in a general way in regard to the possible magnitude of the errors in a system whose rough diagram alone is known except that they are dependent upon the degree of undercooling used and upon the rate of crystallization of the particular substances (i.e., upon the amount of solid separated out), upon the lag in the thermometer registration, and upon the possibility of following either curve below the true eutectic temperature.

SUMMARY

The freezing point-composition diagram for the system β-chlorocrotonic acid–β-chloroisocrotonic acid has been constructed by a rough method in which no correction was made for the amount of solid crystallizing and this diagram as well as the log $N - \frac{1}{T}$ plot for these data have been compared with those obtained from the accurate data It has been shown that the errors involved cause a shift of the observed eutectic not only along the temperature axis, but also along the composition axis In some cases false indications of compound formation may be given

Cooling curves have been described which are a direct proof that it is possible to follow a branch of the temperature-composition diagram to temperatures below the eutectic

The relation between the entropy of fusion and the shape of a branch of the $T - N$ diagram of an ideal binary system has been discussed

An analysis of the causes of increased errors near the eutectic point is made and it has been pointed out that it is dangerous to draw definite conclusions from the abnormalities or distortions in the freezing point diagrams unless the method of obtaining the data eliminates the sources of error mentioned

REFERENCES

(1) Skau and Saxton J Am Chem Soc **50,** 2693 (1928)
(2) Latimer J Am Chem Soc **44,** 90 (1922)
(3) Biltz and Meinecke Z anorg allgem Chem **131,** 1 (1923)
(4) On the basis of the data of Parks, Huffman, and Thomas J Am Chem Soc **52,** 1032 (1930)
(5) Timmermans Bull soc chim Belg **37,** 409 (1928)
(6) Mortimer J Am Chem Soc **44,** 1429 (1922)
(7) Andrews, Kohman, and Johnston J Phys Chem **29,** 914 (1925)
(8) Bell and McEwen Ind Eng Chem **14,** 536 (1922)
(9) Gibson, Duckham, and Fairbairn J Chem Soc **121,** 270 (1922)

THE FREEZING POINT-SOLUBILITY RELATIONS OF GEOMETRICAL ISOMERS. II

THE DYNAMIC ISOMERISM OF THE ANISALDOXIMES

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In a series of articles published about 1900 (1) it was pointed out that certain geometric isomers exhibit the phenomenon known as "dynamic isomerism", i.e., the *cis* and the *trans* modifications tend to transform one into the other until an equilibrium mixture is reached. In those investigations the binary freezing point diagrams for a few such systems were studied and the equilibrium compositions were then estimated by freezing point measurements. If these compositions could be determined with a sufficient degree of accuracy, it should be possible to calculate the heat of transformation of the one modification to the other.

There are many difficulties involved in this method, however, for in many cases the rate of transformation is rapid enough at the melting point so that the composition of the mixture changes very appreciably during the freezing point determination.[2]

Inasmuch as all previous work on such systems was done by the capillary melting point method or at best by the Beckmann apparatus, it seemed of interest to find out what controlled cooling curves and heating curves would show and to test out the applicability of an apparatus previously described (2) to a system of this type. The system, *cis*-β-chlorocrotonic acid–*trans*-β-chlorocrotonic acid, which was reported in the first (2) of this series of papers, showed no signs of "dynamic isomerism" at moderate temperatures. The supposed "unstable equilibrium" of the system, crotonic acid–isocrotonic acid, on the other hand, proved on investigation to be a much more complicated equilibrium phenomenon, probably involving polymerization (3).

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[1] Du Pont Fellow, Yale University, 1924–1925. Part of this paper was written during the tenure of a Guggenheim Fellowship at the Bayerische Akademie der Wissenschaften, Munich, Germany. Present address Trinity College, Hartford, Connecticut.

[2] In fact, in some cases the freezing point and the melting point are different. When the rate of transformation is extremely rapid, the solid obtained upon freezing a liquid mixture of any composition will be one of the modifications in pure form. For a detailed discussion of these interesting possibilities see ROOZEBOOM: Die heterogenen Gleichgewichte, II, Part 3, Vieweg, Braunschweig (1918)

Carveth (4) studied the system, *cis*-anisaldoxime–*trans*-anisaldoxime, and finally came to the conclusion that it was impossible to construct the temperature-composition diagram even roughly. He found that the freezing points could not be determined either for the pure forms or for mixtures by means of a Beckmann freezing point apparatus, owing to the rapid transformation toward a definite equilibrium composition. The freezing point obtained by this method was always in the neighborhood of 54.2°C., which he interpreted as the "natural freezing point" of the system, i.e., the freezing point of the equilibrium mixture. He determined the melting points of the pure substances by the capillary tube method as 62.8°C. and 132°C., respectively, and showed that the less stable, *cis* form would liquefy if kept at 89.5°C. for twelve hours. He concluded that the eutectic was about 0.2° below the "natural freezing point", since that was the lowest temperature he was able to reach by changing the composition and since he was unable to detect a second break in the rough cooling curves which he ran. He attempted to get the melting temperatures of various mixtures of the two forms by means of the capillary tube method, but failed to get even approximately reproducible results. He stated, "It has been found absolutely impossible to obtain with any accuracy the composition of the triple point."

The benzaldoxime system, which was studied by Cameron (5), seemed to exhibit the same phenomena, but in this case it was found possible to construct a rough freezing point-solubility diagram. Since the results of Patterson and MacMillan (6) on the rates of transformation in ethyl tartrate solution show that *cis*-anisaldoxime and *cis*-benzaldoxime are equally stable[3] it seemed that it should be possible to construct the diagram for the anisaldoxime system.

We have found that the cooling curve method is not entirely applicable to the case, but we were finally able to construct the binary freezing point diagram, to follow the transformation involved, and to determine the composition at the "natural freezing point" with a fair degree of accuracy by means of controlled heating curves.

SYNTHESIS AND PURIFICATION OF COMPOUNDS

The *trans*-anisaldoxime was synthesized by Schmidt and Söll's method (7) from anisaldehyde and hydroxylamine hydrochloride in alcohol solution containing a large excess of barium carbonate in suspension.

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[3] Brady and Dunn (J. Chem. Soc. **123**, 1783 (1923)) state that *cis*-anisaldoxime is more stable at atmospheric conditions than *cis*-benzaldoxime.

The yield of crude oxime was 95 per cent. This product was recrystallized repeatedly from methyl alcohol and carbon tetrachloride.

The *cis*-anisaldoxime was prepared from the *trans* modification by Dunstan and Thole's method (8) as modified by Brady and Dunn (9). These authors mention the difficulty of drying the *cis*-oxime. In this particular case we found that the drying of the solid could be omitted if the sample, after being sucked dry on the Buchner funnel, was extracted with boiling benzene, the water layer being reëxtracted. The purification was effected by repeated recrystallization from benzene. The final product melted quite sharply in a capillary tube at about 127°C., the temperature being raised at the rate of about 2° per minute as the melting point was approached.

The apparatus used for running cooling and heating curves has been described elsewhere (2).

EXPERIMENTAL RESULTS AND DISCUSSION

Limitations of cooling-curve method

It was found that, in accordance with the conclusions of Carveth, it was impossible to get the freezing point of either pure modification by means of cooling curves, since there was always a partial transformation to the other form as soon as the melting took place. However, we did find it possible to follow the transformation of the *trans* form to the equilibrium mixture for the system by means of a series of successive cooling curves on a sample of *trans*-anisaldoxime. The first curve was a very rapid one carried out by the method described in another paper (10), that is, by cooling the melt to a temperature just below the freezing point and then inoculating and stirring, the surroundings being at the temperature of the room. The other curves were obtained by the usual method, except that the crystallization took place extremely slowly and the mixture had to be stirred vigorously to cause the rise in temperature to the maximum, whereas ordinarily the maximum is reached without any further stirring after the inoculating crystals have once been stirred into the melt.

The first cooling curve gave a maximum temperature of 60.7°C. (not a "flat"), the second curve, 60.0°C. The sample was then heated to 92°C. and allowed to cool in the course of ten minutes, and the maximum came at 57.5°C. The next curve gave 57.4°C. and the last 57.4°C. A number of cooling curves were run on this sample and the area-maximum plot[4] was made, but the results were not self-consistent, many maxima being decidedly low. From all these results it was estimated that the true primary freezing point of the equilibrium mixture was above 57°C.

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[4] To correct for the solid separated out at the maxima, see Andrews, Kohman, and Johnston: J. Phys. Chem. **29**, 914 (1925).

The heating curve method

Since it was found impossible to obtain satisfactory cooling curves, owing to the rapid rate of transformation, heating curves were used and they proved to be much better adapted.[5]

The same apparatus was used as for cooling curves, but the copper shield was heated at a constant measured rate, the adjustment being made by means of a variable resistance shunted across the heating coil. This served as the only source of heat for the melt, whose temperature was then followed in the usual way. The breaks were in most cases quite sharp and the results in general very consistent. By means of such heating curves it was found possible to obtain the melting point of the pure untransformed *trans*-anisaldoxime and to follow the transformation toward an equilibrium mixture whose freezing point was determined. Since it was also possible to construct the temperature-composition diagram of the binary system using this same method, the composition of the equilibrium mixture was disclosed by its freezing point.

TABLE 1

Successive curves on the same sample of trans-anisaldoxime

CURVE NUMBER	TYPE OF CURVE	RATE OF HEATING (OR COOLING)	POINT *a*	POINT *b*	POINT *c*
			degrees C	*degrees C*	*degrees C*
I	Heating	Medium	—	—	72 5
II	Heating	Medium	56 5	59 9	75 5
III	Heating	Medium	56 5	59 0	72 6
IV	Heating	Medium	56 8	58 6	70 9
V	Heating	Medium	56 4	58 4	76 3
VI	Cooling	Very slow	—	—	—
VII	Heating	Very rapid	56 0	60 0	82 9
VIII	Heating	Very slow	56 2	59 7	67 0
IX	Heating	Medium	56 0	58 7	74 0
X	Cooling	Very slow	—	—	—
XI	Heating	Medium	56 2	59 6	—

Following the transformation by heating curves

A number of *successive* heating curves were run on the same sample of pure *trans*-anisaldoxime. On plotting the data for the first and second runs, two curves of the types shown in figure 1, A and B respectively, were obtained. The straight lines show the change of the temperature of the shield with time and the curved lines below show the corresponding temperatures of the sample. The breaks in these curves and in the rest of the curves, all of which had the same general shape as figure 1, B, have been tabulated in table 1. In figure 1, A, a "flat" was obtained (constant within one microvolt, 0.02°) lasting for eight minutes at the temperature 62.6°C., which is, therefore, the melting point of pure *trans*-anisaldoxime. The second curve, of the type shown in figure 1, B, is decidedly different. There is a partial flat, presumably at the eutectic temperature (point *a*), at the end of which there is a sharp change in direction, and later there is a second break (point *b*) after which the temperature rises rapidly to the temperature of the shield. Point *b* corresponds to the temperature where the last crystal disappears or to the primary freezing point of the mixture. These points were determined by plotting the time-deviation curves, the deviation being the difference between the temperature of the shield and that of the melt at any given time. The breaks are thus much more marked. Point *c* is the highest temperature to which the sample was raised before cooling and running the next curve.

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[5] The heating curve method is not suggested as a general method for determining accurate freezing points of binary mixtures. It is much less satisfactory when the primary freezing point is far removed from the eutectic temperature.

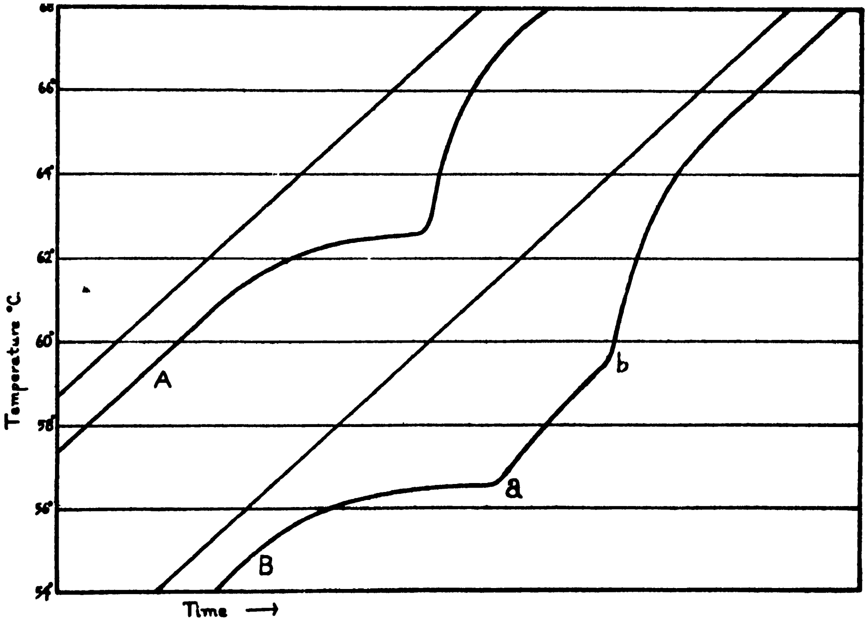

FIG. 1. TYPICAL SUCCESSIVE HEATING CURVES OF A SAMPLE OF PURE *trans*-ANISALDOXIME

A number of interesting facts are brought out by this series of curves. In the first place, it shows that the heating curve method is vastly superior to the Beckmann freezing point method. This follows from Carveth's statement (4) that after heating the pure *trans*-anisaldoxime to 64°, 100°, or 125°C. for thirty minutes, the primary freezing points could not be distinguished from the "natural freezing point", namely, 54.2°C. In spite of the fact that in the course of runs I, II, and III the temperature was kept well above 64°C. for about fifty minutes in each case, the resulting mixtures were very definitely distinguishable from the equilibrium mixture. The fact that the eutectic temperature *a*, was a little lower in the later curves indicates that this heating had caused a slight oxidation or decomposition of the oxime.

A study of the table also shows that the natural freezing point is probably on that side of the eutectic nearer the pure *trans* form.

The rise in point *b* after curve VI is perhaps also worthy of notice. This seems to be explained best by assuming that it was due to the slow cooling of the melt in curve VI; that is, that as the solid *trans* form separated at the "natural freezing point", and the liquid thus became richer in the *cis* form, transformation took place toward the reestablishment of the equilibrium composition in the liquid, so that the resulting solidified melt contained less of the *cis* form. This is verified by the fall in *b* for the next two curves and a rise again after another cooling curve, X.

TABLE 2

Freezing points for the binary system, cis-anisaldoxime–trans-anisaldoxime

Cis	T_1	T_2	T_3	T_E
per cent	*degrees C*	*degrees C*	*degrees C*	*degrees C.*
0	62.6			
4.23	60.8	60.6		56.4, 56.6
7.62	59.5			56.3
10.61	58.6	58.5		56.6, 56.6
14.79	57.8			56.8
19.48	56.7	56.6	56.8	56.7, 56.2, 56.4
22.76	(64)			56.6
33.63	(80)			56.6
100.00	127*			

* Melting point by capillary tube method.

Construction of the temperature-composition diagram

The various compositions were made by intimately mixing the pulverized crystals of the two forms in the right proportions on a small piece of plate glass and then transferring to the freezing point tube. The thermoelement was then inserted in the well-packed sample and the whole was put into the freezing point apparatus without first melting. The heating curve obtained in each case was of the type shown by figure 1, B.

In all cases the melt was immediately chilled as soon as the point *b* had been passed and a second heating curve was run on the solidified material.

Thus, the least possible time was allowed for transformation to take place, and the second curve usually checked the first one to within 0.3°C. when the temperature of melting was not much above 60°C. On the *cis*-side of the curve, however, the transformation seemed to be much more rapid

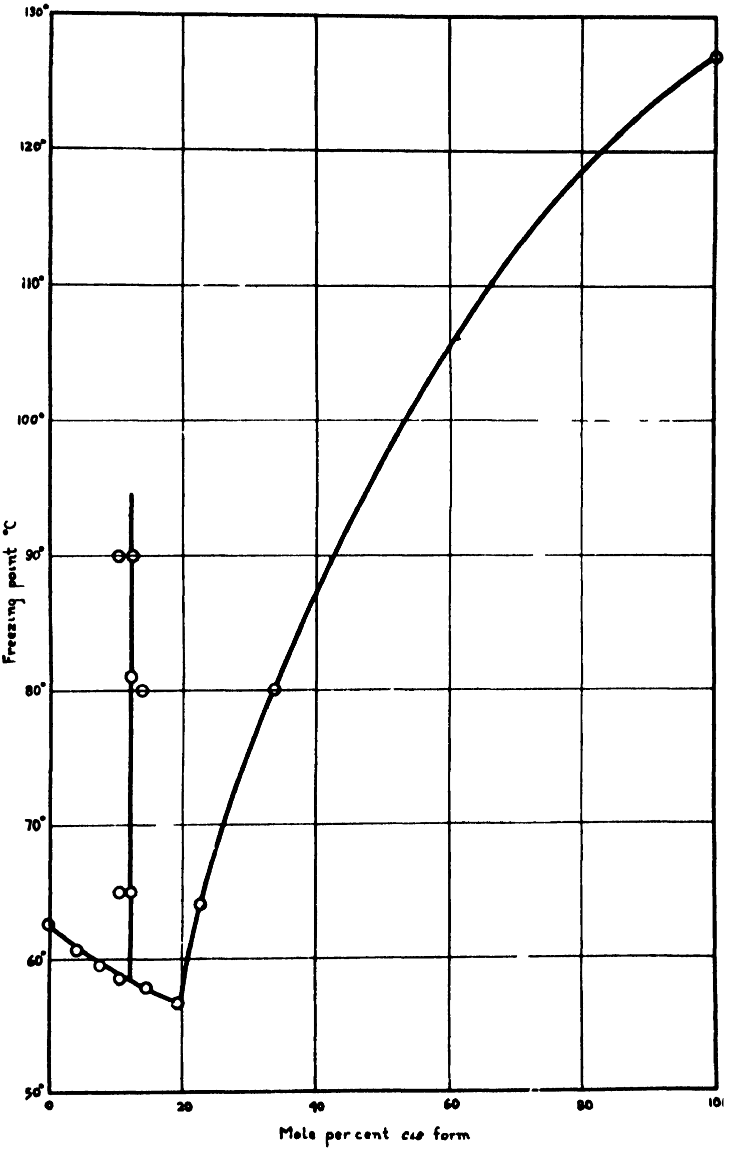

Fig 2. Freezing Point-Composition Diagram for the System, *cis*-Anisaldoxime–*trans*-Anisaldoxime

and the freezing points for this branch are, therefore, probably as much as 2°C. too low. The second curves in these cases failed to check the first ones; for example, the curves for the 22.76 per cent mixture gave the freezing points 64° and 58.9°C., respectively, and the 33.63 per cent sample gave the freezing points 80°C. for the first and 58.3°C. for the second curve.

The data obtained from these curves are given in table 2 and are plotted in figure 2. The values obtained for point *b* in successive curves on the same sample are designated by T_1, T_2, and T_3, and the corresponding values obtained for the eutectic temperature, T_E, are given in their respective order. It was impossible to get the melting point of the pure *cis* form by any but the capillary-tube method (see below) and thus this value may be in error by 3° or 4°C. since the value obtained depends to a considerable extent on the rate of heating. The eutectic temperature, obtained by averaging all the values for T_E, is 56.5°C. The eutectic composition, gotten by extrapolation of the two arms of the binary freezing point curve, is about 19.5 per cent *cis*- and 80.5 per cent *trans*-anisaldoxime.

The formation of another compound above 100°C.

The successive heating curves obtained for a sample of the pure *cis* form prove that the transformation is not so simple as the one suggested by Carveth, that is, to an equilibrium mixture of the *cis* and *trans* modifications, but that some other substance or substances are formed. In the first curve the shield was started at 121.6°C. and raised about 0.5°C. per minute. The unmelted sample of *cis*-anisaldoxime, which was at room temperature when inserted, rose very rapidly to 106.6°C., then dropped to 100.1°C. (indicating a considerable absorption of heat), and then rose without any further breaks to 132°C. The sample was then chilled to room temperature and a second curve run on it. This showed a eutectic flat at 39.5°C., about 17°C. below that found for the binary eutectic above, and then a rise toward the temperature of the shield, the last crystals disappearing at about 49.5°C. In another case in which the first heating was carried up to 140°C., the second and third heating curves gave eutectic flats at 39.2°C. and 39.0°C., respectively. In both of these cases the final sample was decidedly yellow in color. On the other hand, the mixture of anisaldoximes containing 33.63 per cent of the *cis* form (see table 2) gave the normal eutectic break, at 56.6°C., even though it had been subjected during a previous curve to a temperature of over 80°C. The facts seem to indicate that at about 100°C. or over, another compound is formed.

It was actually found possible to isolate this compound in crystalline form from mixtures obtained by heating the pure *trans* form to corresponding temperatures. (1) A small amount of the pure *trans* form was heated in a sealed evacuated tube at 125°C. It first became yellow, then red, and when finally removed from the oven, after forty-eight hours, it was deep reddish brown in color and long needle-like crystals separated at a high temperature. The primary freezing point of the mixture was about 129°C. It was found that a slightly yellow crystalline compound could be precipitated from the alcohol solution of the mixture by adding the right amount of water. Without further purification this compound melted in a capillary tube at 168–172°C. to a brown liquid. (2) Another sample heated at 110°C. for a number of months did not discolor to as great an extent. In this case there were some well formed yellow crystals at the top of the tube, evidently deposited by sublimation, which gave a melting point of 160–166°C. without purification. The formation of the compound is accompanied by the evolution of ammonia,[6] judging from the development of considerable pressure in the tube and from the distinctive odor and the action on litmus paper of the gas evolved.[7] At higher temperatures there seems to be a distinct odor of tertiary amines.

The composition of equilibrium mixtures at various temperatures

The formation of the compound in the neighborhood of 100°C. and above makes it impossible to follow the binary equilibrium mixture above that temperature. Unfortunately this narrows the possible range of study of the change of equilibrium composition with the temperature to a 30° range between the "natural freezing point" and about 90°C.

A number of samples of *trans*-anisaldoxime and of mixtures with the *cis* modification were heated at various temperatures in sealed tubes. Their freezing points were then determined by means of heating curves and their compositions estimated by comparison with the binary freezing point diagram. The values obtained are tabulated in table 3 and have been included in figure 2.

The results show that, owing to the short temperature range permitted, a more sensitive method than the one at hand will have to be used to determine with sufficient accuracy the slope of the equilibrium curve.

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[6] It was noticed that when pure *trans*-anisaldoxime was left for some time in a desiccator over sulfuric acid, the exposed surface of the sample became slightly yellow. As this was not investigated further, we are unable to say whether it was due to the formation of the yellow compound isolated.

These observations are quite similar to those of West (J. Am. Chem. Soc. **47**, 2780 (1925)) on the aldoxime of 4,6-dicarbethoxyl-5-formyl-3-methyl-2-cyclohexenone. He found that water and ammonia were evolved when the aldoxime was heated for twenty to thirty minutes at 100°C. under a pressure of 20-30 mm. He also observed that "when dried in a vacuum desiccator for eighteen hours over sulfuric acid the compound lost weight (water and ammonia (?)) and passed into a substance that began to turn brown at 126°C. and melted at 140°C. with decomposition."

Hurd (The Pyrolysis of Carbon Compounds, p. 660 ff., The Chemical Catalog Co., New York (1929)) cites several cases in which ammonia is evolved on heating ketoximes.

[7] This reaction is now being studied further.

The values for the individual samples show very good agreement among themselves and the freezing points of the equilibrium mixtures obtained by heating the pure *trans* form fall within 0.15°C. of their mean value, 58.4°C. For some reason, however, the mixtures obtained by approaching equilibrium from the other side do not show the same good agreement.

It should be noted that in approaching the equilibrium from the *trans* side of the diagram the freezing point drops to the value for the equilibrium mixture, whereas in approaching it from the *cis* side, the freezing point drops to the eutectic point and then rises to its final value. Thus in the case of the 33.63 per cent *cis* mixture at 80°C., where the duration of heating was only one and one-half hours, the final freezing point was low and this may have been due to the fact that the transformation was incomplete. It seems probable, however, that true equilibrium was reached in all the other cases, for sufficient time was allowed and the results showed good agreement, except that the mixtures approached from the *cis* side gave values about 0.5°C. higher than expected—most likely owing to the fact that for some unknown reason the breaks in the heating curves were actually much less distinct and that therefore the freezing point could not be determined with the same degree of accuracy. It seems logical therefore to give more weight to the values for the equilibrium mixtures which were obtained by heating the pure *trans* form.

TABLE 3

Change of "equilibrium" composition with temperature

COMPOSITION OF ORIGINAL PER CENT OF *cis* COMPOUND	HEATING		POINT *a*	POINT *b*
	Temperature	Duration		
	degrees C	*hours*		
0	90	12 5	56 1	58.2
			56 2	58 3
26 22	90	73	56 5	58 9
0	81	47	56 5	58 5
			56 7	58 4
33 63	80	1 5	56 6	(57 9)*
0	65	50	56 4	58 3−
			56 5	58 3+
22 76	65	69	55 9	58 9

* Probably not yet at equilibrium.

On this basis, the data of table 3 show that the freezing point of mixtures which have been brought to equilibrium at temperatures between 65°C. and 90°C. is 58.4°C. ± 0.2°, corresponding to a composition of 12.3 per cent of the *cis* and 87.7 per cent of the *trans* form. This value is in accord with the data of table 1.

SUMMARY

The "dynamic isomerism" in the *cis*-anisaldoxime–*trans*-anisaldoxime system has been investigated. The binary freezing point-composition diagram of this pair of geometric isomers was constructed and was then used as a basis for a method of analysis of unknown mixtures.

Owing to the rapid rate of transformation in the liquid state toward the equilibrium composition, it was found necessary to substitute a controlled heating curve method for the usual cooling curve method, although it was found possible to follow the transformation roughly by means of the latter.

When either form is heated to about 100°C. or above, a reaction takes place involving the formation of a compound which has been isolated. The study of the change of the simple binary equilibrium with temperature is thus limited to a narrow range between about 60°C. and 90°C.

The "natural freezing point" of the simple binary system was found to be 58.4°C. ± 0.2°C., corresponding to a composition of 12.3 per cent of the *cis* form. This equilibrium composition did not change perceptibly with the temperature up to 90°C.

REFERENCES

(1) Duhem: Z. physik. Chem. **22**, 545; **23**, 193, 497 (1897).
Bancroft and coworkers: J. Phys. Chem. **2**, 143, 159, 245, 364, 376, 409 (1898); **3**, 144, 437 (1899).
(2) Skau and Saxton: J. Am. Chem. Soc. **50**, 2693 (1928).
(3) Skau and Saxton: J. Am. Chem. Soc. **52**, 335 (1930).
(4) Carveth: J. Phys. Chem. **3**, 437 (1899).
(5) Cameron: J. Phys. Chem. **2**, 409 (1898).
(6) Patterson and MacMillan: Proc. Phil. Soc. Glasgow (1911); Brit. Chem. Abstracts **100**, i, 648 (1911).
(7) Schmidt and Söll: Ber. **40**, 4257 (1907).
(8) Dunstan and Thole· Proc. Chem Soc. **27**, 233 (1911).
(9) Brady and Dunn: J. Chem. Soc. **123**, 1783 (1923).
(10) Skau and Saxton: J. Phys. Chem. **37**, 183 (1933).

STUDIES IN AUTO-OXIDATION. III

THE INITIAL ACT IN AUTO-OXIDATION[1]

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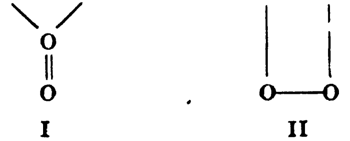
Although peroxide formation is quite generally accepted as the initial step in auto-oxidation, much debate has centered around the question as to whether the isolable peroxide is actually the primary addition product or whether there is first formed a more active and unstable substance, which rearranges into the isolable compound.

This question was first raised by Engler and Weissberg (1), following the observation that benzaldehyde, dissolved in benzene together with indigo, and exposed to oxygen, decolorized the indigo much more rapidly than the same concentration of benzoylhydroperoxide, in the same solvent, exposed to an atmosphere of carbon dioxide. This observation seemed to indicate that, during the process of auto-oxidation, there was formed a more active intermediate than the isolable benzoylhydroperoxide.

At the time when this observation was made, it was, of course, impossible to draw the necessary distinction except on the basis of two distinct compounds. In view of our present knowledge of activated molecules, however, it seems unnecessary to assume any difference, other than one of energy content, between the freshly formed peroxide and the known compound. At the moment of formation the energy-rich molecules would be expected to be much more efficient in the destruction of the indigo than would the normal molecules of the same substance.

A conclusion similar to that of Engler and Weissberg was reached later by Staudinger in connection with his work on the ketenes and, in particular, on the basis of some work of Erdman (2) upon which Staudinger (3) commented. According to the latter, the addition of oxygen to the ethenoid linkage yields, as a primary product, a highly active, unsymmetrical peroxide, or *moloxide* (I), which may later rearrange into the more stable, symmetrical compound (II).



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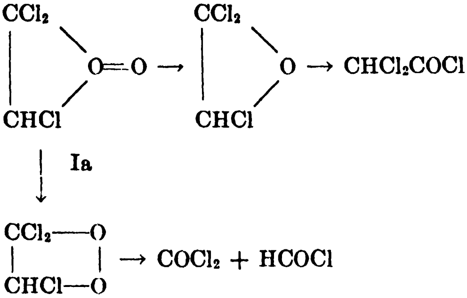
[1] **Presented at the 15th annual Canadian Chemical Convention at Hamilton, Ontario, June 1 to 3, 1932.**

In support of this viewpoint, it is pointed out that the products obtained by Erdman from trichloroethylene can be most simply accounted for by assuming that the "moloxide" (Ia) is, in part, reduced to the oxide and, in part, isomerizes to the normal peroxide (IIa).



IIa

This argument, however, appears unconvincing to the present writer, as the oxide would be a normal product of the interaction of peroxide with the original substance (4).

Quite recently, Jorissen and Van der Beek (5) have revived the question of the nature of the initial peroxide as a result of an observation on the oxidation of benzaldehyde in the dark, presumably at room temperature. Under these conditions a strong peroxide test was obtained, although it had been shown previously (6) that in direct sunlight no peroxide survived. The authors state that their peroxide could not have been benzoylhydroperoxide, otherwise it would have reacted with the benzaldehyde. Finally, the conclusion is drawn that the substance is probably the primary addition product of oxygen and the aldehyde, which may later revert to the isolable benzoylhydroperoxide.

The interpretation given by these authors to their experimental evidence seems to the present writer to be inconsistent with one of their own observations, namely, that exposure to direct sunlight of a mixture partially oxidized in the dark resulted in the destruction of the peroxide in a few minutes. The fact that the peroxide survived in the dark need only be ascribed to the difference in its rate of reaction with benzaldehyde in the dark and in direct sunlight, as Bäckström (7) has already shown that the reaction between benzoylhydroperoxide and benzaldehyde is sensitive to light in the near ultra-violet. There seems every indication, therefore, that the peroxide obtained by the dark reaction is benzoylhydroperoxide. Again, the assumption that the primary product is a substance of weaker oxidizing ability (lower energy content) than benzoylhydroperoxide is one which can hardly be justified thermodynamically, as the primary product should be richer in energy than the substance into which it rearranges.

The most recent attempt to revive the conception of a structural difference between the primary peroxide and the isolable product is found in the recent papers of Milas (8), whose theory is based on his interpretation of recent work in band spectroscopy by Mulliken (9), Birge (10), and others. This evidence indicates clearly that diatomic molecules of the type of CO, CO^+, BO, BeF, CN, etc., possess electrons in excess of eight which behave essentially as the valence electrons of atoms. The explanation advanced by Mulliken and by Birge (11) is that the two nuclei, together with their *K* electrons, are enclosed in a common shell of eight, with the remaining electrons in an outer shell. Such outer electrons might properly be designated as "molecular valence electrons."

To outline briefly some of the main assumptions underlying Milas' theory, the following might be mentioned:

(1) Auto-oxidation is assumed to be possible "only when the auto-oxidants possess unshared or 'exposed' electrons." These unshared electrons are referred to as "molecular valence electrons," the inference being that they are, in all cases, essentially similar to the valence electrons of diatomic molecules of the type mentioned above (12).

(2) These unshared electrons are assumed to have their spins unpaired and to be more loosely bound to the molecule than shared pairs (reference 12, p 299).

(3) The first change assumed to take place in any auto-oxidation is a change in energy level of these "molecular valence electrons." That is, electronic activation is assumed to be a necessary preliminary to all auto-oxidations (reference 12, p. 299).

(4) A pair of such electrons already raised to some higher energy level is then assumed to be donated to the oxygen molecule, with the formation of a "dative" peroxide.

(5) The "dative" peroxide rearranges into the more stable peroxide or undergoes other reactions

For the sake of brevity and convenience may we examine these assumptions in order.

(1) The present writer knows of no evidence from band spectroscopy or from any other source that would indicate that all unshared electrons may be properly regarded as "molecular valence electrons." To take one typical example as an illustration, that of aldehydes, the carbonyl group might be considered as a pseudo-atom, having its valence electrons shared with hydrogen and organic radical, respectively. However, there seems no reason for assuming, with Milas, that unshared oxygen electrons in such molecules are capable of behaving as valence electrons.

(2) The assumption that the spins of such unshared electrons are not paired would seem to require some justification in order to carry weight against the current opinion that they are paired. Likewise, there seems

some need of substantiation for the assumption that these electrons are more loosely bound to the molecule than others.

(3) Most, if not all, auto-oxidations are thermal reactions. It is true that light is apparently universally effective in accelerating these reactions, but they are not exclusively photochemical. It seems entirely improbable, then, that electronic activation is a necessary preliminary to auto-oxidation, for electronic excitation levels lying below the visible part of the spectrum are very rare. In any event, excitation of oxygen electrons in ethers and aldehydes (reference 12, pp. 352–5) seems quite impossible in view of the fact that the lowest excitation level of oxygen is of the order of 8 volts.[2] In spite of this fact, however, Milas assumes an excitation of oxygen electrons in the water molecule by supersonic vibrations (reference 12, p. 317). For the frequency in question, 750,000 cycles, the corresponding energy of activation would be 3×10^{-9} volts, or approximately 7×10^{-5} calories per mole!

(4) The donation of a pair of "molecular valence electrons" to the oxygen molecule is represented through the use of the following electronic structure for oxygen

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}} :$$

As oxygen is known to have zero electric moment (13), this cannot represent the normal oxygen molecule. If it represents an electronically activated state there seems no possible way of accounting for the energy of activation in thermal reactions. It should be pointed out further in this connection, that the electronic structures used for some of the donor molecules are subject to similar criticisms. For example, the structure for ethylenic compounds

$$\mathrm{R} : \overset{\cdot\cdot}{\mathrm{C}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}} : \mathrm{R}_1$$

cannot be considered as representing the normal molecules, as the electric moment of ethylene is known to be zero (14). If it represents an electronically activated state there seems to be no place for such a structure in the representation of auto-oxidations which are thermal reactions.

(5) In the foregoing pages it has been shown that there exists no acceptable evidence in favor of the existence of two structurally different forms of the peroxide; therefore the conception of the "dative peroxide," "moloxide," or any other hypothetical intermediate seems to serve no useful purpose.

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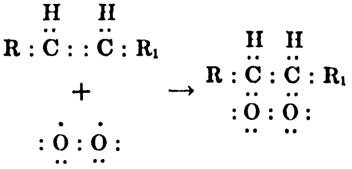
[2] This, I think quite justifiably, leaves out of the question the metastable level at 1.65 volts, which apparently has a very low probability of formation by direct absorption of light.

THE MODE OF ACTIVATION IN AUTO-OXIDATIONS

In view of the fact, already mentioned, that auto-oxidations in general are thermal reactions, it seems necessary to exclude any such energetic activation as that postulated by Milas. Vibrational activation appears to be quite sufficient to account for experimental facts. It cannot be denied, of course, that when such reactions are hastened by photochemical means electronic activation must occur. However, as there is no evidence indicating that the use of light changes the primary step in the reaction, it seems safe to assume that the accelerating effect of light is due to the increase in vibrational energy following the absorption of a quantum of light. It will, therefore, be assumed in this paper that all auto-oxidations involve the primary addition of oxygen to a linkage which has been activated by vibration, whether the necessary vibrational level has been attained purely by thermal means or by absorption of light.

Ethenoid compounds

In the case of compounds containing the ethenoid linkage it is quite easy to understand, on the basis of conventional structures, the vibrational weakening of one of the bonds between the two carbon atoms and the pairing of the two odd oxygen electrons at this point. The preferred structure for the oxygen molecule is that of G. N. Lewis (15), since it is the only one which is in agreement both with the paramagnetism and the absence of electric moment. Using electronic structures the addition of oxygen would be represented in the following manner.

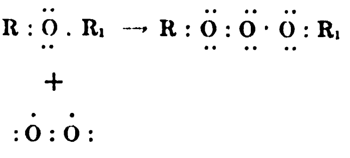


$$\begin{array}{c} \mathrm{H}\qquad\mathrm{H} \\ \mathrm{R} : \ddot{\mathrm{C}} : : \ddot{\mathrm{C}} : \mathrm{R_1} \\ + \\ : \dot{\mathrm{O}} : \underset{\cdot\cdot}{\dot{\mathrm{O}}} : \end{array} \longrightarrow \begin{array}{c} \mathrm{H}\qquad\mathrm{H} \\ \mathrm{R} : \ddot{\mathrm{C}} : \ddot{\mathrm{C}} : \mathrm{R_1} \\ : \underset{\cdot\cdot}{\ddot{\mathrm{O}}} : \underset{\cdot\cdot}{\ddot{\mathrm{O}}} : \end{array}$$

The addition of oxygen to the $C{\equiv}C$ bond may be considered in a similar manner.

Ethers

It is well known that ethers, on pyrolysis, usually undergo rupture adjacent to the ether oxygen. It is evident then, that the C—O linkage is the weak point in the molecule. Addition of oxygen to ethers would, therefore, be represented as follows:

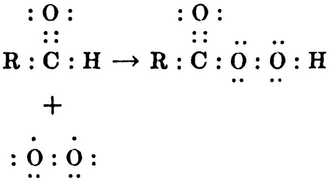


$$\begin{array}{c} \mathrm{R} : \underset{\cdot\cdot}{\ddot{\mathrm{O}}} \,.\, \mathrm{R_1} \\ + \\ : \dot{\mathrm{O}} : \dot{\mathrm{O}} : \end{array} \longrightarrow \mathrm{R} : \underset{\cdot\cdot}{\ddot{\mathrm{O}}} : \underset{\cdot\cdot}{\ddot{\mathrm{O}}} \cdot \underset{\cdot\cdot}{\ddot{\mathrm{O}}} : \mathrm{R_1}$$

In this case the original linkage consists of only one electron pair instead of two, as in the case of ethenoid compounds. Hence the addition of oxygen at this point effects a complete separation of the atoms sharing that pair.

Aldehydes

In the case of aldehydes, the facility with which dehydrogenation takes place justifies the assumption that the weakest linkage in simple aldehyde molecules must be the C—H bond. Therefore, the addition of oxygen would be expected to take place at this point through pairing of the odd oxygen electrons with carbon and hydrogen respectively.

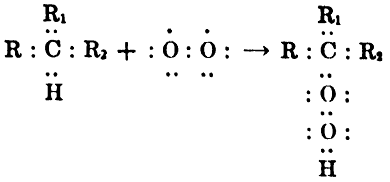


$$\begin{matrix} :O: & & :O: \\ :: & & :: \\ R:C:H & \rightarrow & R:C:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}:H \\ + & & \\ :\overset{.}{\underset{..}{O}}:\overset{.}{\underset{..}{O}}: & & \end{matrix}$$

Saturated hydrocarbons

The fact that saturated hydrocarbons are auto-oxidized offers an instance of the complete failure of the general theory of Milas, as these compounds possess no "molecular valence electrons." In his most recent publication Milas recognizes this fact and proposes a special mechanism to fit this particular case (reference 12, page 346). This mechanism is essentially the one which follows from the viewpoint developed in the present paper.

In the case of the paraffins, it is evident from the work of Pope, Dykstra, and Edgar (16) that oxidation tends to take place on the terminal carbon atom of the longest open chain. On the other hand, the oxidation of the alkyl benzenes has been shown by the writer to take place at the carbon atom alpha to the ring (17). The apparent discrepancy in these results, is, of course, due to the well-known fact that hydrogen attached to the alpha carbon atom in the alkyl benzenes is abnormally reactive. In each of the above cases, as well as in other recent investigations (18), the oxidations have been thermal reactions, which fact necessarily precludes electronic activation. According to the theory developed in this paper the oxygen molecule would be expected to attach itself at the bond most susceptible to vibrational activation. At the time of writing, the evidence seems to indicate that the C—C bond has a lower energy of dissociation than the C—H bond; therefore the former would be expected to be preferentially attacked. However, recent work (19) indicates that the difference in the above dissociation energies is very small; therefore, it seems quite possible that the weakest C—H bond in a given hydrocarbon molecule might have a lower energy of dissociation or activation than the weakest C—C bond. In any event, it is quite obvious that C—H bonds are usually attacked in preference to C—C bonds. The initial act in the auto-oxidation of saturated hydrocarbons would then be represented by the following scheme:



$$\begin{array}{ccc} \mathrm{R_1} & & \mathrm{R_1} \\ \mathrm{R : \ddot{\underset{..}{C}} : R_2} + \mathrm{:\dot{\underset{..}{O}}:\dot{\underset{..}{O}}:} & \longrightarrow & \mathrm{R : \ddot{\underset{..}{C}} : R_2} \\ \mathrm{H} & & \mathrm{:\underset{..}{O}:} \\ & & \mathrm{:\underset{..}{O}:} \\ & & \mathrm{H} \end{array}$$

where R_1 and R_2 might represent hydrogen and / or hydrocarbon radical, depending on whether the hydrocarbon was a paraffin (16), an alkyl benzene (17), or an alkyl cyclane (18b, 18c).

Miscellaneous compounds

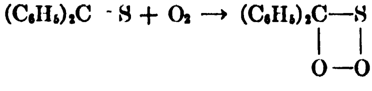
The foregoing illustrations deal with only a limited group of compounds, but it seems to the writer unnecessary to multiply examples by discussing in detail other types. However, brief mention might be made of two additional examples, which are of some interest. One of these compounds, thiobenzophenone, has been the subject of recent controversy as to the point in the molecule at which oxygen adds (20; and 10, p. 328).

Thiobenzophenone is an unstable substance which decomposes at 160–170°C. in the following manner:

$$2(C_6H_5)_2C{=}S \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2S$$

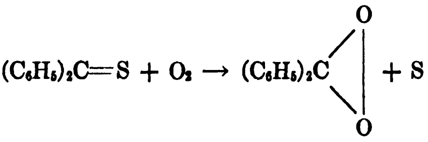
The oxidation products obtained by Staudinger and Freudenberger were benzophenone, sulfur and small amounts of sulfur dioxide; the fact that the latter appeared only in small amounts led them to the belief that the oxygen added to the carbon atom. Milas, in dissenting from this viewpoint, represented the initial act as the addition of oxygen to the sulfur atom, implying, as in other cases, an electronic activation.

It seems evident, from the ease with which thiobenzophenone is decomposed thermally, that the assumption of electronic activation of this substance is unnecessary to account for its auto-oxidation. From the point of view developed in the present paper the oxygen would be expected to add at the linkage of least thermal stability, which is obviously the C=S linkage,



$$(C_6H_5)_2C{=}S + O_2 \longrightarrow \begin{array}{c}(C_6H_5)_2C\text{—}S \\ \quad\quad\quad\;\; | \quad\; | \\ \quad\quad\quad\;\; O\text{—}O\end{array}$$

However, in this case, the complete rupture of the double bond in the C=S group takes place so easily that it seems probable that the oxygen molecule obtains both the necessary electrons from the carbon atom, forming an alkylidene peroxide and liberating sulfur.



The appearance of only traces of sulfur dioxide would indicate such a small amount of side reaction that we need not concern ourselves with its nature.

The second compound of interest belongs to a general class mentioned by Milas (21) as typical examples of compounds possessing "molecular valence electrons." Triethylphosphine possesses an unshared pair of phosphorus electrons and Milas assumes, with other previous workers, that the addition of oxygen takes place at that point. However, the experimental evidence on the subject seems entirely at variance with this viewpoint (22). Leaving aside the reactions that take place in the presence of water, it has been found that the main isolable product of the oxidation of the dry substance is the compound,

$$(C_2H_5)_2PO\ OC_2H_5$$

Now, the simplest explanation of the origin of this compound is on the basis of initial formation of the peroxide

$$(C_2H_5)_2P\ O\ O\ C_2H_5$$

which might rearrange in a very obvious manner to give the above diethyl phosphinic ester. Therefore, it seems reasonable to conclude again that the oxygen attaches itself at a vibrationally activated bond, in this case the carbon-phosphorus bond.

A comparison of the mechanism of auto-oxidation reactions suggested in the present paper with those presented by Milas reveals the fact that the initial stage of the present writer corresponds with the second stage of Milas in all cases except the last two mentioned. The formation of the intermediate peroxide in auto-oxidations is thus considered as a single act rather than as consisting of two stages. As has already been implied, this does not mean that no distinction is recognized between the freshly formed peroxide molecules and the normal molecules of isolable product. A difference in energy content admittedly does exist, but there appears to be no reason for associating this with a structural difference which can be represented by any present system of notation.

REFERENCES

(1) Engler and Weissberg: Kritische Studien über die Vorgänge der Autoxydation, p. 90. Braunschweig, 1904.
(2) Erdman: J. prakt. Chem. **85**, 78 (1913).
(3) Staudinger: J. prakt. Chem. **85**, 330 (1913).
(4) Lenher: J. Am. Chem. Soc. **53**, 3737 (1931).
(5) Jorissen and Van der Beek: Rec. trav. chim. **49**, 138 (1930).
(6) Jorissen and Van der Beek: Rec. trav. chim. **45**, 245 (1926).
Van der Beek: Rec. trav. chim. **47**, 286 (1928).
(7) Bäckström: Medd. Vetensk. Acad. Nobelinst. [6] **16**, 15 (1927).
(8) Milas: J. Phys. Chem. **33**, 1204 (1929); Chem. Rev. **10**, 295 (1932).
(9) Mulliken: Proc Nat. Acad. Sci. **12**, 144 (1926).
(10) Birge: Nature **117**, 300 (1926).
(11) See also Langmuir: J. Am. Chem. Soc. **41**, 868 (1919); Grimm: Z. Elektrochem. **31**, 474 (1925); Glockler: Proc. Nat. Acad. Sci. **12**, 522 (1926).
(12) Milas: Chem. Rev. **10**, 298–9 (1932).
(13) Smyth: Dielectric Constant and Molecular Structure, p. 85. Chemical Catalog Co., New York (1931).
(14) Smyth and Zahn: J. Am. Chem. Soc. **47**, 2501 (1925).
(15) Lewis, G. N.: Chem. Rev. **1**, 243 (1924).
(16) Pope, Dykstra, and Edgar: J. Am. Chem. Soc. **51**, 2203 (1929).
(17) Stephens: J. Am. Chem. Soc. **48**, 1824, 2930 (1926); **50**, 186, 2523 (1928).
(18) (a) Brunner and Rideal: J. Chem. Soc. **1928**, 2324.
(b) Chavanne: Bull soc. chim. Belg. **36**, 206 (1927).
(c) Chavanne and Bode: J. Am. Chem. Soc. **52**, 1609 (1930).
(d) Mondain-Monval and Quanquin: Compt. rend. **191**, 299 (1930); Ann. chim. [1] **15**, 309 (1931).
(19) Mecke: Nature **125**, 526 (1931).
(20) Staudinger and Freudenberger: Ber. **61**, 1836 (1928).
(21) Milas: J. Phys. Chem. **33**, 1211 (1929).
(22) Engler and Weissberg: Ber. **31**, 3055 (1898).

THE pH OF GELATIN SOLUTIONS

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The authors are led by the recent paper of Hartman and Fleischer (1) to make the following comments.

The pH of a solution is theoretically rather poorly defined, since the idea of concentration has lost its early significance. The usual accepted methods of determination and comparison are useful and satisfactory in many cases, but as is well-known they are subject to influences which more or less invalidate the results obtained. Thus, the hydrogen electrode is usually considered the most fundamentally sound, with the colorimetric methods subject to errors due to influences such as salt, alcohol, and proteins It is therefore surprising to come upon an article where the colorimetric methods are given preference over the electrometric methods. In such a case substantial proof would appear to be necessary before the conclusions can be accepted.

Hartman and Fleischer have determined the pH of gelatin solutions by several methods. These included the use of two sets of colorimetric buffers and indicators, the use of the hydrogen and quinhydrone electrodes, and the use of the glass electrode, although in this latter case the pH values were not determined, as sufficient data was lacking.

With the colorimetric methods the values agreed, but with the electrometric methods, especially in the case of the hydrogen electrode, variation with time was enormous. With the quinhydrone electrode the values obtained at different times agreed well, but did not agree with the values obtained colorimetrically. The results obtained with the glass electrode varied with time, but not to the same degree as shown by the hydrogen electrode.

The authors have had occasion to determine the pH of gelatin solutions over a rather wide range in connection with a study of the dielectric constant and dispersion in gelatin solutions. They have used the glass electrode as a means of making these determinations and have no reason to doubt the accuracy of the records obtained. A vacuum tube voltmeter using the FP 54 tube and following the general lines of Hill's apparatus (2), was constructed through the coöperation of Prof H. H. Willard. The apparatus was shielded by means of metal boxes and the grid circuit was insulated by means of amber. The electrodes were constructed after the specifications of MacInnes and Dole, using for the membranes the special Corning glass .015 manufactured for this purpose. Saturated calomel was used as a reference electrode. In all cases two glass electrodes were used and the connection to the grid was changed from one to the other by means of a long glass rod so as to avoid polarization effects while the electrode shielding cage was open. The electrodes were calibrated against standard buffers and it was found that a linear relation was approximated. The readings on any solution could be changed to pH by means of this calibration. That no drifting occurs may be seen from the determinations (see table 1) made of the pH of a solution of Eastman's isoelectric gelatin and distilled water at widely different times. These values were taken only with the idea in mind of getting an accuracy of about 0.1 pH. Therefore recalibration of the electrodes each day was not made as is essential in very accurate work. However, if the glass electrodes vary as stated by Hartman and Fleischer, it is hardly conceivable that they will vary together, therefore the authors give the following values, taken consecutively and without the added refinements that would go with determinations of pH in other connections. These are stated without regard for the content of gelatin acid or alkali, the pH having been changed by the addition of hydrochloric acid or sodium hydroxide.

TABLE 1

The pH of a solution of isoelectric gelatin

GEL	pH AS GIVEN BY ELECTRODE	
	1	2
per cent		
0 5	4 70	4 69
1 0	4 70	4 60
1 0	4 68	4 61
0 5	4 69	4 65

2 72	2 71
5 67	5 75
4 67	4 70
5 86	5 88
8 20	7 29
4 19	4 20
3 68	3 64
3 96	3 91

It would be possible to continue, as the authors have some hundred such determinations. In the list, there appears to be only one case where a pH disagreement of more than .1 is found, namely, with 7.08 and 6.96.

It has been found by Ferguson (4) and his students as well as by others that the pH values determined by the hydrogen electrode are reproducible and constant.

The authors are fully aware that mere agreement does not constitute a sound basis establishing the fundamental accuracy of a method They do not at this time contend that the values obtained in gelatin solutions give the proper measure of the hydrogen-ion activity They do however contend that, properly used, the glass electrode will give definite and reproducible values in gelatin solutions and, as contrasted with colorimetric determinations, the presumption of accuracy is in favor of the electrometric methods.

REFERENCES

(1) HARTMAN AND FLEISCHER J Phys Chem **36**, 1136 (1932)

(2) HILL Science **73**, 529 (1931)

(3) MACINNES AND DOLE Ind Eng Chem , Anal Ed **1**, 57 (1929)

(4) FERGUSON AND SCHLUCHTER J Gen Physiol **15**, 463 75 (1932)

CATAPHORESIS. AN IMPROVED CYLINDRICAL CELL

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Received October 13, 1932

In a previous issue of This Journal (2) the author described a cylindrical cataphoresis (electrophoresis) cell for the ultramicroscopic determination of the speed of electrical migration and of the isoelectric point of colloidal materials. A formula for calculating the electrosmotic velocity distribution of the liquid in the cylindrical tube was also given.

This cell has proven very useful in a series of investigations dealing with the isoelectric precipitation of a number of complex precipitates such as silicates, phosphates, humates, and proteinates of aluminum and iron (3); also ferrocyanides, sulfides and hydroxides, and a number of other amphoteric colloids (5, 3). In the course of this work it was found possible to improve the cell in regard to one important point. It is the object of this paper to describe the present construction of the cell and also, in response to several inquiries, to present the derivation of the formula expressing the electrosmotic flow of the liquid.

The new form of the cell is shown in figure 1. The cell represents an almost straight tube, the slope of the electrode compartments being merely sufficient to cause a free outflow of the liquid and to permit the latter of being sucked into the cell without leaving any air bubbles behind. The great advantage in this form is that the cell can be effectively cleaned, which is very important. This is done by pulling a thread through the cell by means of a thin copper wire covered with insulating material to prevent scratching. A little cotton is tied onto the thread, which is then pulled back and forth in the tube which has been filled with a soap solution or other cleaning liquid. This effectually removes any deposit on the glass.

To make this procedure possible the electrodes had to be so placed as to be out of the way. The writer is indebted to the Glass Blowing Department of Eimer and Amend for finding a way out of the difficulty. The electrodes, which must have a large surface to prevent the formation of gas bubbles up to as high a concentration as possible, have been fused on to the walls of the conically shaped electrode compartments. This has proven to be very satisfactory.

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The diameter of the tube is the same as that of the older type and should be about 2.5 mm. The distance between the electrodes should be such as to yield a potential gradient of about 10 volts per centimeter. At this potential and a magnification of from 100 to 150 diameters, the migration of the particles becomes sufficiently rapid for accurate measurements. A higher potential gradient is avoided because this lowers the upper limit of concentration of the electrolyte. Without the use of non-polarizable electrodes we are, even at this potential, limited to a salt concentration of about 0.02 normal. In the case of strong acids and bases this upper limit lies still lower. At higher concentrations gas is evolved at the electrodes and causes displacement of the liquid.

This limitation of the cell is however compensated for by its simplicity and the rapidity with which measurements can be made. Since the charge on colloidal particles is very sensitive to the influence of ions, it seldom happens that higher concentrations of electrolytes are employed. This is especially true of the amphoteric systems studied by the writer. These are precipitated from very dilute solutions and, except in the very rare cases where the system is isoelectric at very low or very high pH, no difficulties from the evolution of gas are encountered. Such difficulties can, however, within certain limits be overcome by reducing the potential gradient to five or less volts per centimeter. The particles then move more slowly in proportion and make the measurement less accurate.

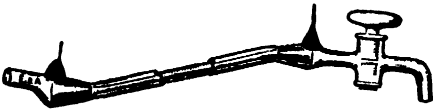

FIG. 1. CYLINDRICAL CATAPHORESIS CELL

The cell is connected directly to the terminals of a D. C. generator, to a series of storage cells, or to dry cells. It can be ordered in any length according to the available voltage.

It is extremely important that the stopcock at the lower end of the cell be kept well greased so as to completely close the tube. The particles must show no movement when the circuit is open.

The optical combination consists of a Bausch and Lomb 8 mm. (21×) objective and a 5 or 7.5 ocular. The working distance of this objective is 1.6 mm., which is sufficient for a focus at the proper depth of the cell (see below). In measuring the diameter of the tube in terms of microscope scale divisions, a 16 mm. objective having a working distance of 7 mm. is employed as previously described.

In place of the more complicated system of illumination originally employed by the writer, a simple illumination unit consisting of a 16 mm.

objective, a system of condensing lenses, and a 6-volt Mazda lamp, all mounted in a single tube and adjustable by rack and pinion in three directions, has been adapted by the Arthur H. Thomas Company, Philadelphia, Pa., and by Eimer and Amend, New York City, for use in connection with the cell here described.

In the preceding article on this subject the electrosmotic flow of the liquid in a *closed* cylindrical tube of the type here described was explained and illustrated. At the boundary between the glass wall and the liquid there exists an electrical double layer. If the glass is negatively charged (as it usually is except when coated with positive colloids) then the liquid is positive and is attracted along the boundary to the negative electrode.[2]

Since now the cell is closed it is obvious that as much liquid as flows along the boundary in one direction must return through the center of the tube in the opposite direction. In an annular layer somewhere between the wall and the axis of the tube the liquid must therefore be at rest.

The following expression for the velocity V of the liquid in the different parts of the tube was given

$$V = c\left(r^2 - \frac{a^2}{2}\right)$$

where r = the distance from the axis of the tube,
a = the radius of the tube, and
c = a constant determined by the P D of the double layer.

From this expression it follows that $V = 0$ where

$$r = a\sqrt{\tfrac{1}{2}} = a \times 0.707$$

When we measure the cataphoretic movement of the particles in a closed cylindrical tube we must therefore focus the microscope at a depth of 0.3 (0.293) of the radius below the inner wall (or roof) of the tube, for only then will the observed velocity of the particles be equal to their true velocity. Owing to a steep velocity gradient of the liquid and to the depth of the focus, this condition is only approximately fulfilled. Thus the different particles visible in the field never move with exactly the same velocity.

The derivation of the formula for which the writer is indebted to Dr. Hilding Faxèn of the University of Upsala is as follows. The velocity distribution in a cylindrical tube obeys the law

$$V = c\,(r^2 - C) \qquad (1)$$

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[2] In reality the layer of liquid immediately next to the glass does not move, as this constitutes the inner electrical layer and remains fixed to the glass. The thickness of this innermost layer is undoubtedly much less than a micron, probably only a few millimicrons. In a tube of 2.5 mm. diameter we can therefore ignore the thickness of this film.

where r = the distance from the axis of the tube, and c and C are constants (1, 4).

Where the motive force acts as a difference in pressure at the ends of the tube, as is ordinarily the case, then the movement is all in one direction and is greatest along the axis, whereas at the wall of the tube the liquid does not move at all. In this case $C = a^2$, where a = the radius of the tube.

But in electrosmose the motive force acts along the surface layer, causing a flow of liquid next to the wall of the tube. Since the tube is closed, the same amount of liquid must return through its center. This is mathematically expressed by the formula

$$\int_0^a Vr dr = 0 \tag{2}$$

The formula assumes this simple form through the rotation symmetry.

With the value of V inserted and integrated

$$c\left(\frac{a^4}{4} - C\frac{a^2}{2}\right) = 0 \tag{3}$$

we get

$$C = \frac{a^2}{2}$$

By putting $\frac{a^2}{2}$ in place of C in formula 1 we get

$$V = c\left(r^2 - \frac{a^2}{2}\right) \tag{4}$$

which is the expression employed.

For comparison the corresponding four expressions in the theory of Smoluchowski (6), which applies to a closed chamber between two plane parallel plates (the kind of cell used by all other investigators), will be given.

For a chamber the plates of which are the distance $d = 2a$ apart we have

$$V = c(x^2 - C) \tag{1a}$$

x = the distance from the middle

$$\int_{-a}^{+a} V dx = 0 \tag{2a}$$

$$2c\left(\frac{a^3}{3} - Ca\right) = 0 \tag{3a}$$

$$C = \frac{a^2}{3}$$

$$V = c\left(x^2 - \frac{a^2}{3}\right) \tag{4a}$$

Hence in this type of cell $V = 0$ where

$$x = \frac{a}{\sqrt{3}} = a \times 0\,577 \ldots$$

These expressions take no account of the influence of the side walls of the chamber on the electrosmotic flow of the liquid. They are therefore only applicable when the sides of the chamber are very far apart in proportion to the depth. The cylindrical cell employed by the writer allows therefore a more exact mathematical expression of the velocity distribution.

REFERENCES

(1) Lamb, H.: Hydrodynamics, 5th edition No. 331, Cambridge University Press, London (1930).

(2) Mattson, Sante: J. Phys. Chem. **32**, 1532–52 (1928).

(3) Mattson, Sante: The laws of soil colloidal behavior. III. Soil Sci. **30**, 459–95 (1930). IV. Soil Sci. **31**, 57–77 (1931). V. Soil Sci. **31**, 311–31 (1931). VII. Soil Sci. **33**, 41–72 (1932). Isoelektrische Niederschlage und ihre Eigenschaften, in Kolloid-Z. **58**, 305–14 (1932).

(4) Mises, R. von: Elemente der Theorie der Hydromechanik, Vol. I, pp. 36–40. Samml. math. phys. Schriften, von E. Jahnke, Leipzig (1914).

(5) Parbery, N. H., and Mattson, Sante: Soil Sci. **33**, 75–94 (1932).

(6) Smoluchowski, M. von.: Graetz, Handbuch Elektr. Magn. **7**, 383 (1921).

PERIODIC PRECIPITATION OF FERROUS CARBONATE

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INTRODUCTION

In a previous article of This Journal, "The Liesegang Phenomenon Applied to the Lake Superior Iron Formations" (1), a synthetic demonstration of the Lake Superior iron formation is presented. Silica gels were prepared by mixing ammonium carbonate and sodium silicate solutions. Over these gels were placed solutions of ferrous ammonium sulfate of various strengths. There resulted in the gel bands of ferrous carbonate. In the text of this article is cited the fact that the same banded structure might occur if a silica gel prepared from carbon dioxide and sodium silicate solution were employed. Also, it is proposed that with this gel ferrous sulfate might yield bands as good as those obtained with ferrous ammonium sulfate.

It is the purpose of this investigation to study further the periodic precipitation of ferrous carbonate in different gels, thus substantiating the theory of formation of the Lake Superior iron formations proposed in the previous article. The facts cited in this paper as well as those of the former article tend to support the geologic theories proposed by C. R. Van Hise and C. K. Leith (2) concerning the origin of this formation.

EXPERIMENTAL

From approximately one hundred different experimental preparations, the eighteen showing the most outstanding periodic precipitation are pictured in figure 1. Each tube was filled about two-thirds full with the gel and covered with about 7 cc. of iron salt solution.

The first horizontal row of test tubes (A) contains gels prepared from 4 per cent gelatin solution. The tubes, A1 and A2, contain 4 per cent gelatin solution made 0.1 N with respect to sodium carbonate, A3 and A4, 0.5 N with respect to ammonium carbonate, A5 and A6, 0.5 N ammonium carbonate and also containing 5 per cent glucose by weight. The tubes A1 and A2 were covered with 0.8 N and 0.4 N ferrous ammonium sulfate solution, respectively, A3 and A4 also with 0.8 N and 0.4 N ferrous ammonium sulfate solution, respectively, A5 with 0.4 N ferrous sulfate, and A6 with 0.4 N ferrous ammonium sulfate.

In the horizontal rows B and C the gels were prepared from sodium silicate solution (sp. gr. 1.03) by bubbling carbon dioxide gas through the silicate solution for varied lengths of time. This was accomplished by passing the gas through the silicate solutions contained in the test tubes (12 cc.) at the rate of 4.7 liters per hour. The carbonate content of the gels was governed by the length of time that the gas was allowed to bubble

FIG. 1

The flow meter used to measure the rate of flow of the carbon dioxide gas was similar to that described in a previous article (3). In standardizing and using the flow meter, however, kerosene was used in place of water.

Gels B1, B2, and B3 were prepared by passing carbon dioxide gas at the rate of 4.7 liters per hour through sodium silicate solution (sp. gr. 1.03) for three, four, and five minutes, respectively; gels B4, B5, and B6 were prepared by bubbling the carbon dioxide gas for four minutes. In all cases in row B the gels were covered with ferrous ammonium sulfate solution. In B1, B2, and B3 the solution covering the gel was 0.3 *N* while the gels in B4, B5, and B6 were covered with *N*, 0.8 *N*, and 0.5 *N* solutions, respectively.

The gels in row C were prepared in a manner exactly analogous to the corresponding gels in row B. The gels in C1, C2, and C3 were each covered with 0.8 *N* ferrous sulfate solution; C4, C5, and C6 were covered with *N*, 0.5 *N*, and 0.3 *N* ferrous sulfate solutions, respectively.

All the ferrous salt solutions were changed each day for three days and then every other day until three more displacements had been made. Following this they were permitted to stand three weeks with a replacement of the solution once each week. The photograph was taken at this time.

DISCUSSION

A comparison of the bands produced in row A with either row B or C shows that the gels made from gelatin shown in row A were decidedly inferior for the production of bands. The gels made from gelatin (row A) produce less well-defined bands than those pictured in rows B and C where silica gel was the diffusing medium. This is probably due to the fact that gelatin offers a decidedly different diffusing medium than the silica gels. It appears, therefore, that the distinct banding of ferrous carbonate is specific for silica gels.

In comparing A1 and A2 in which the gels were made 0.1 *N* with respect to sodium carbonate and covered with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate, respectively, it can be seen that the strength of the ferrous salt solution covering the gel seems to have no effect on the ferrous carbonate banding. This same conclusion may be drawn in A3 and A4, where the gels were made 0.5 *N* with respect to ammonium carbonate and covered with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate solutions, respectively. Comparing A3 and A4 with A1 and A2 it is seen that ammonium carbonate in place of sodium carbonate in the gel tends to decrease the banding effect obtained in A1 and A2 and more even diffusion (A3, A4) occurs. The addition of 5 per cent glucose to a gel made from gelatin which is 0.5 *N* with respect to ammonium carbonate seems to decrease the formation of ferrous carbonate bands and to increase diffusion, as is evident in the comparison of tube A6 with A4.

A5, which is identical with A6 except that the gel is covered with ferrous sulfate in place of ferrous ammonium sulfate, demonstrated the same diffusion effect as is produced in A6.

Of the first three tubes in row B, the one containing the gel (B2) prepared by bubbling carbon dioxide for four minutes through the sodium silicate solution (sp. gr. 1.03) showed the deepest diffusion and the most distinct banding of ferrous carbonate. (B1, B2, and B3 were covered with 0.3 *N* ferrous ammonium sulfate solution.) For this reason gels prepared by bubbling carbon dioxide for four minutes were placed in tubes B4, B5, and B6 and were covered with *N*, 0.8 *N*, and 0.5 *N* ferrous ammonium sulfate solutions, respectively. Of these three gels (B4, B5, and B6) the gel covered with normal ferrous ammonium sulfate solution gave the best banding of ferrous carbonate.

A comparison of the tubes of row C indicates that gels covered with 0.8 *N* ferrous sulfate (C1, C2, and C3) give much better banding than the other tubes of that row. These experiments show conclusively that better banding is obtained when the carbon dioxide–sodium silicate gels are covered with solutions of ferrous sulfate (row C) rather than ferrous ammonium sulfate (row B).

A number of experiments were conducted using 2 per cent agar-agar gels made 0.5 *N* with respect to ammonium carbonate and sodium carbonate. Some of these gels also contained sucrose and glucose. These gels were covered with both 0.4 *N* and 0.8 *N* ferrous ammonium sulfate solutions. In all these experimental preparations very marked and rapid diffusion resulted with no banding whatsoever.

Carbon dioxide–sodium silicate gels were also prepared from sodium silicate solutions of specific gravity 1.06 and 1.10 and covered with the iron salt solutions of various strengths. A very dense impervious layer of ferrous carbonate was deposited on the surface of the gel after a very slight diffusion, thus preventing any further diffusion or banding. The gels made from these denser sodium silicate solutions were quite opaque.

Gels prepared from sodium silicate of densities less than 1.03 were not firm enough for any practical experiments. Likewise, iron salts of less than 0.3 *N* strength did not cause banding to any extent. Saturated solutions of these salts also resulted in no marked banding effect in the gels.

Tube C1 shows the best banding of ferrous carbonate of any herein pictured. The gel employed here was prepared by bubbling carbon dioxide through sodium silicate solution. Ferrous sulfate solution covered the gel. This, then, shows conclusively that the peculiar banding of the iron formations could have been brought about by the slow diffusion of ferrous sulfate (or, perhaps some other ferrous salt) as well as ferrous ammonium sulfate into a gel formed by the interaction of carbon dioxide, as well as basic nitrogenous substances or carbonates, with sodium silicate solution.

REFERENCES

(1) Hartman and Dickey: J. Phys. Chem **36**, 1129–35 (1932).
(2) Van Hise and Leith: U. S. Geol. Survey, Monograph 52.
(3) Hartman and Brown: J. Phys. Chem. **34**, 2651–65 (1930).

A METHOD FOR A MORE COMPLETE EXAMINATION OF BINARY LIQUID MIXTURES

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The customary examinations of liquid mixtures (either isothermal or isobaric) have been time-consuming and tedious enough, almost to prevent an exhaustive study of any particular mixture. Theoretical chemistry and the industries dealing with distillation and solvents have alike required an extension of the information available at the present. The study of zeotropic or azeotropic mixtures and their pressure-temperature-composition equilibria, requires a far greater fund of data than the literature affords. It would be desirable to have at hand not only a single isothermal investigation or two, but a "matte" of data from which we could construct at will any desired isobaric or isothermal diagram. Changes in the vapor pressure-temperature equilibria at constant composition in the liquid phase could be plotted from such data, and the heats of vaporization for any desired composition, pressure, and temperature combination could be calculated. Such a matte would allow an examination of the changes in the activity coefficients with the several variables of the system, and would permit predictions for any desired conditions or point (*P*-*T*-*N*). These predictions are one of the prime purposes of any investigation. It is the purpose of this paper to present a method of securing sufficient quantities for any system by a more simplified and direct means.

APPARATUS

Figure 1 illustrates the apparatus used by the author. The distillation flask was of somewhat new design, permitting a rapid equilibrium to be reached between the liquid and vapor phases. The flask, which contained the main volume of the sample being studied, was made from a 500-cc. round-bottomed Pyrex flask. The condenser was, as far as the author was able to ascertain, of new design. It consisted of an inner cooling tube against which the vapors impinged. This was sealed within the outer condenser wall but was left open at the top to permit of a variety of cooling methods. It was stoppered and a continual flow of water used, or if necessary, it could be filled with dry ice and ether. Various other refrigerants may also be used. This permits distillations even at fairly low temperatures. The condensate from the vapor phase flowed through a sampling trap and back into the liquid phase. The sampling tube for the liquid phase and the thermometer were placed in the ground glass stopper used for filling the flask. This stopper was securely held by a rubber-covered wire saddle. While no superheating was experienced in the apparatus, it can be prevented by etching the inside bottom of the flask with water glass (1). In order to prevent fractionation of the vapors before passing into the condenser, the upper half of the flask and the throat above it were insulated with asbestos rope wrapping. Control of the pressure was effected by a modified Victor Meyer mercury column regulator which could be rapidly changed in order to serve for control of pressures both above and below atmospheric. The pressure was adjusted to the desired point by raising or lowering the depth of the glass tubing in the mercury. Two large bottles of 4-liter capacity were included to increase the effective volume, thus preventing any noticeable fluctuation in the pressure during operation.

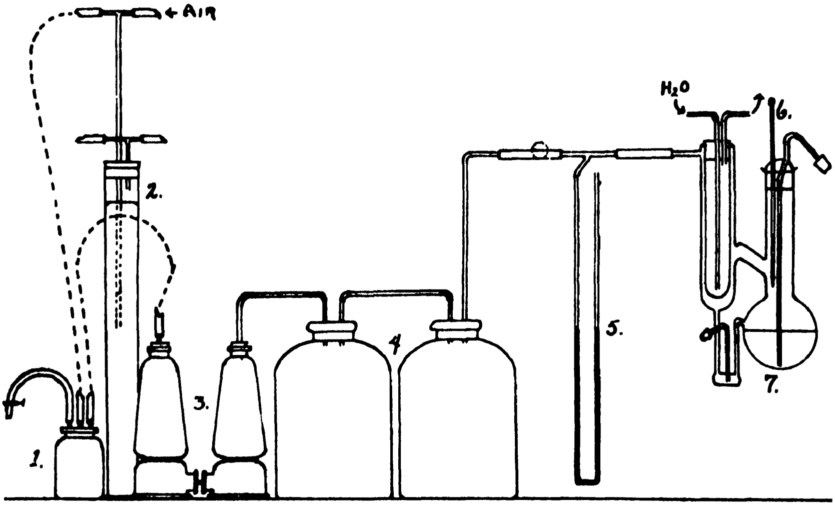

FIG. 1. APPARATUS USED IN THE EXAMINATION OF BINARY LIQUID MIXTURES
1, trap; 2, pressure regulator; 3, drying towers; 4, buffer bottles; 5, manometer; 6, thermometer; 7, distillation flask.

PROCEDURE

The system selected was toluene-ethyl alcohol. This selection was made partly because of previous work upon it (2), and because of the characteristics exhibited over the temperature range used and the ease with which it permitted the use of the refractometer as a means of analysis of the samples. Eleven samples, exclusive of the pure liquids and distributed over the range in composition, were made up from purified liquids. Each sample contained about 300 cc. The sample was placed in the flask and the pressure adjusted to the lowest value, the solution heated to boiling and given a half hour to reach equilibrium. Ordinarily, however, equilibrium was reached in five to ten minutes. A constant thermometer reading was taken as the criterion of equilibrium. The distillation rate was regulated and noted by counting the drops falling from the bottom of the cooling tube in the condenser. The rate was regulated until the condensate in the trap changed completely in a minute's time. The pressure and temperature were noted and the distillation stopped, and the pressure in the apparatus allowed to come to atmospheric level by use of the pinchcock. (Caution must be used when the pressure within the apparatus is greater than atmospheric. In this case the solution must be given time to cool sufficiently to prevent boiling when the pressure is released.) Dried air was forced into the apparatus to blow out samples of the condensed vapor phase and the liquid phase. These were analyzed by means of an Abbé refractometer and the remainder of the samples returned to the flask. The pressure was then adjusted 8 cm. higher and the process repeated on the same sample in the flask until the desired pressure range had been covered.

No trouble was experienced with changing composition of the liquid phase by removal of the samples for analysis. The relative amounts removed were too small to be of any consequence. The same procedure was followed, of course, for each succeeding mixture. This procedure gave the variations in the pressure and the temperature and the change in the composition in the vapor phase in equilibrium with a non-variant liquid phase. Variation in the liquid phase was accomplished only by changing the sample under investigation.

TREATMENT OF DATA

The changes in vapor pressure with temperature for each sample were plotted as shown in figure 2, the pressure in millimeters being given on the ordinate and the temperature on the abscissa. It will be seen that this curve is similar to the vapor pressure curve for a pure liquid. The dotted line represents the composition of the vapor phase in equilibrium, at the various temperatures, with a liquid phase of constant composition, the mole fraction being plotted on the ordinate. In the system of ethyl alcohol–toluene, the change in the vapor composition above any sample was slight, and linear in relationship to the temperature. Best line values were then read from the graph and used to construct tables 1 and 2.[1]

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[1] While the data given in the tables are given to the nearest millimeter, a more recent study of the accuracy of the apparatus indicates that vapor pressures are correct to one-tenth of a millimeter.

From such a graph as figure 2, then, the vapor pressure and the composition of the vapor phase in equilibrium with the liquid phase for that sample can be determined at any desired temperature. Since this plot gives any minute variation in the pressure and the temperature, a plot such as figure 3 can be constructed. Figure 3 is a group of isotherms whose values were read from the graphs of type figure 2. The vapor phase curves in figure 3 have been omitted in all cases excepting that for the 80°C. isotherm.

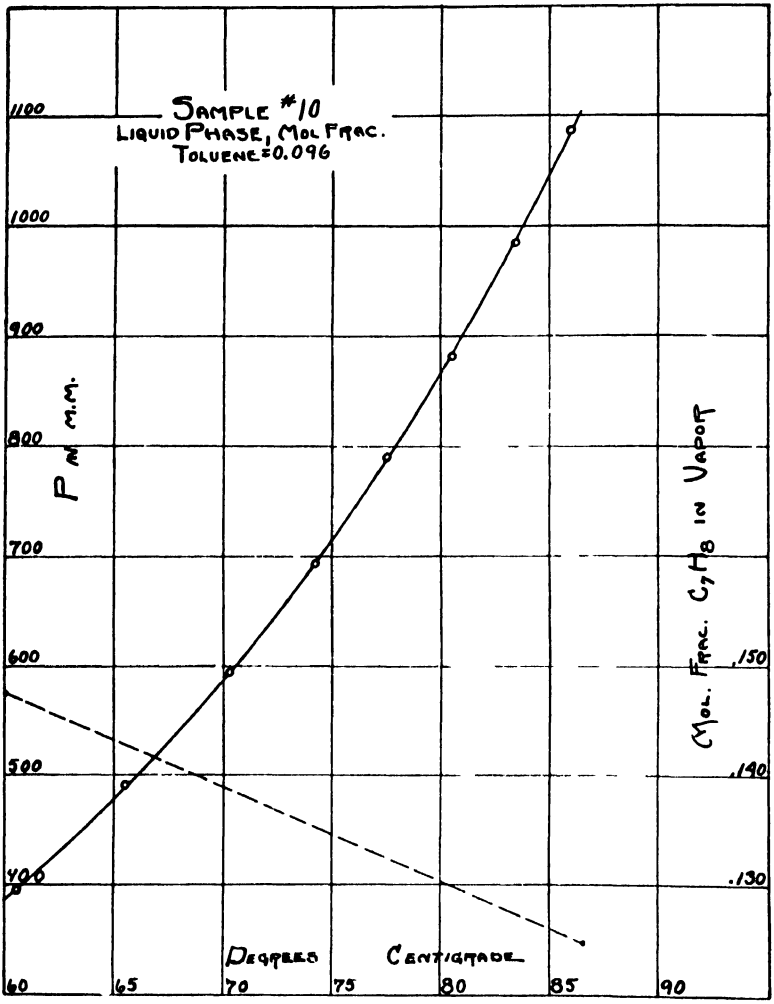

FIG. 2. CHANGES IN VAPOR PRESSURE WITH TEMPERATURE
Sample No. 10; mole fraction of toluene in liquid phase = 0.096

TABLE 1

Isotherms for the system toluene–ethyl alcohol

MOLE FRACTION TOLUENE		TOTAL PRESSURE	PARTIAL PRESSURE
Liquid	Vapor		
75°C.			
		mm	
1 000	1 000	244	
0 893	0 380	444	169
0 769	0 307	677	208
0 648	0 286	688	197
0 557	0 280	698	195
0 457	0 269	707	190
0 375	0 253	715	181
0 274	0 232	722	167
0 233	0 217	724	157
0 155	0 180	724	130
0 096	0 135	716	96 7
0 043	0 075	699	52 4
0 000	0 000	666 1	0
80°C.			
1 000*	1 000	289 7	
0 893	0 379	537	204
0 769	0 301	818	246
0 648	0 271	832	226
0 557	0 270	844	228
0 457	0 262	856	224
0 375	0 245	864	212
0 274	0 223	874	195
0 233	0 209	877	183
0 155	0 175	880	154
0 096	0 130	868	113
0 043	0 074	848	62 8
0 000	0 000	812 6	0
85°C.			
1 000	1 000	397 0	
0 893	0 379	642	243
0 769	0 294	990	291
0 648	0 266	1005	267
0 557	0 260	1016	264
0 457	0 257	1027	264
0 375	0 236	1037	245
0 274	0 215	1047	225
0 233	0 200	1052	211
0 155	0 169	1052	179
0 096	0 126	1047	132
0 043	0 073	1026	74.9
0 000	0 000	986 3	0

TABLE 2

Isotherms for the system toluene–ethyl alcohol

MOLE FRACTION TOLUENE		TOTAL PRESSURE	PARTIAL PRESSURE
Liquid	Vapor		
		60°C	
		mm	
1 000	1 000	139 5	
0 893	0 382	240	91 7
0 769	0 325	367	119
0 648	0 317	373	118
0 557	0 310	382	118
0 457	0 289	387	112
0 375	0 277	390	108
0 274	0 256	395	101
0 233	0 242	397	96 0
0 155	0 198	397	78 6
0 096	0 147	388	57 1
0 043	0 078	375	30 0
0 000	0 000	352 7	0
		65°C	
1 000	1 000	166	
0 893	0 381	301	115
0 769	0 319	455	145
0 648	0 307	466	143
0 557	0 300	472	141
0 457	0 282	477	139
0 375	0 269	481	129
0 274	0 248	486	120
0 233	0 234	487	114
0 155	0 192	488	93 8
0 096	0 143	480	68 7
0 043	0 077	466	35 9
0 000	0 000	436 9	0
		70°C	
1 000	1 000	202 4	
0 893	0 380	367	139
0 769	0 314	557	175
0 648	0 297	569	169
0 557	0 290	572	166
0 457	0 276	584	161
0 375	0 261	590	154
0 274	0 240	592	142
0 233	0 226	598	135
0 155	0 186	598	111
0 096	0 139	591	82 2
0 043	0 076	575	43 7
0 000	0 000	542 5	0

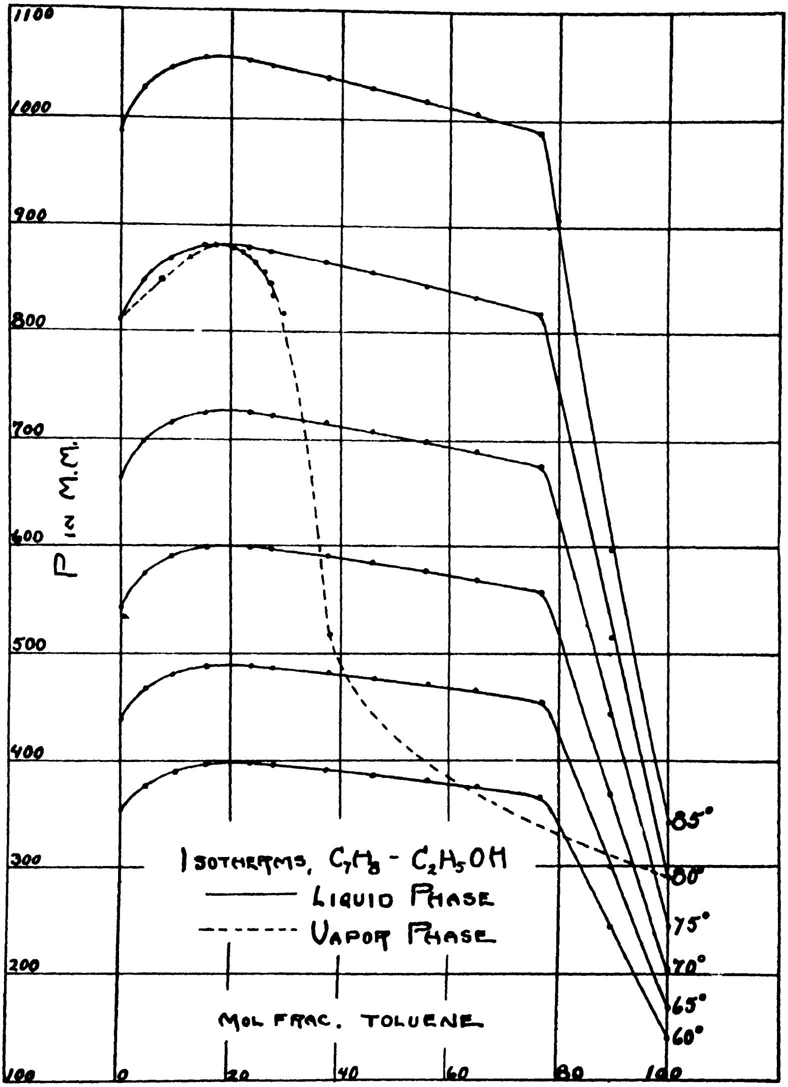

FIG. 3. ISOTHERMS FOR TOLUENE-ETHYL ALCOHOL

It would be advantageous to give an example of the above use of the graphs. If the isotherm at 80°C. is desired, we proceed as follows:

On figure 2, representing sample No. 10, we see that the composition of the liquid phase in mole fraction of toluene is 0.096. At 80°C., we find on referring to the curve that the total pressure on the system is

862.5 mm. This we plot on figure 3 for the isothermal diagram at 80°C., plotting the pressure against the mole fraction of toluene. The dotted line on figure 2 indicates that at the temperature of 80°C., the composition of the vapor phase in equilibrium with the liquid phase for sample No. 10 is 0.130. This, too, is then plotted on figure 3. We then proceed in a similar manner with each of the remaining samples distributed over the range of mixture, and thus determine the complete isothermal diagram for the system at that particular temperature.

DISCUSSION

If the logarithm of the vapor pressure is plotted against $1/T$ for each sample as shown in figure 4, the result is a straight line similar to the plot for a pure liquid. It will be recognized immediately that this is of great value, since the data can be extended by means of the straight line to any desired temperature or used for interpolation between values. The logarithms of the partial pressures of the constituents were then plotted against $1/T$ as in figure 5, and the straight line was again obtained. This is to be expected, for if the total pressure plot gives a straight line, the two partial plots must do likewise.

Data from Sameshima (3) and Cunaeus (4) for the system, acetone–ethyl ether, were plotted in a like manner and similar straight lines were found. Some data given by Schmidt (5) were also applied to such methods of plotting. In the system of benzene–carbon tetrachloride, the straight line relationships held true. The data for the system of benzene–toluene given by Schmidt were found to contain errors in the determination of the vapor pressures. The data given for the vapor pressures of pure toluene would not give a straight line when log P was plotted against $1/T$. Errors in the same direction were found to exist throughout the system at the same temperature.

In the case of toluene-ethyl alcohol, the system was azeotropic, while the system of acetone–ethyl ether and that for benzene–carbon tetrachloride were zeotropic. Evidently the principle holds for either type of liquid mixture. It becomes evident then, that the investigation of a binary liquid mixture requires only the determination of two pressure-temperature-composition diagrams to completely outline the system. This could be most rapidly accomplished by determining two isobaric diagrams.

Since the ethyl alcohol–toluene mixture is azeotropic, having a maximum in vapor pressure, a plot as in figure 4 gives some lines which are located higher than the line for the pure alcohol. However, the lines are not parallel, but vary between the slopes of the lines for the pure liquids and vary as the composition of the liquid phase is varied. Examination shows that the maximum occurs at a composition which changes with the temperature. If the straight lines were extended sufficiently, eventually all would lie within the lines for the pure liquids. At the temperature at which this occurs, the system becomes zeotropic. In this particular case,

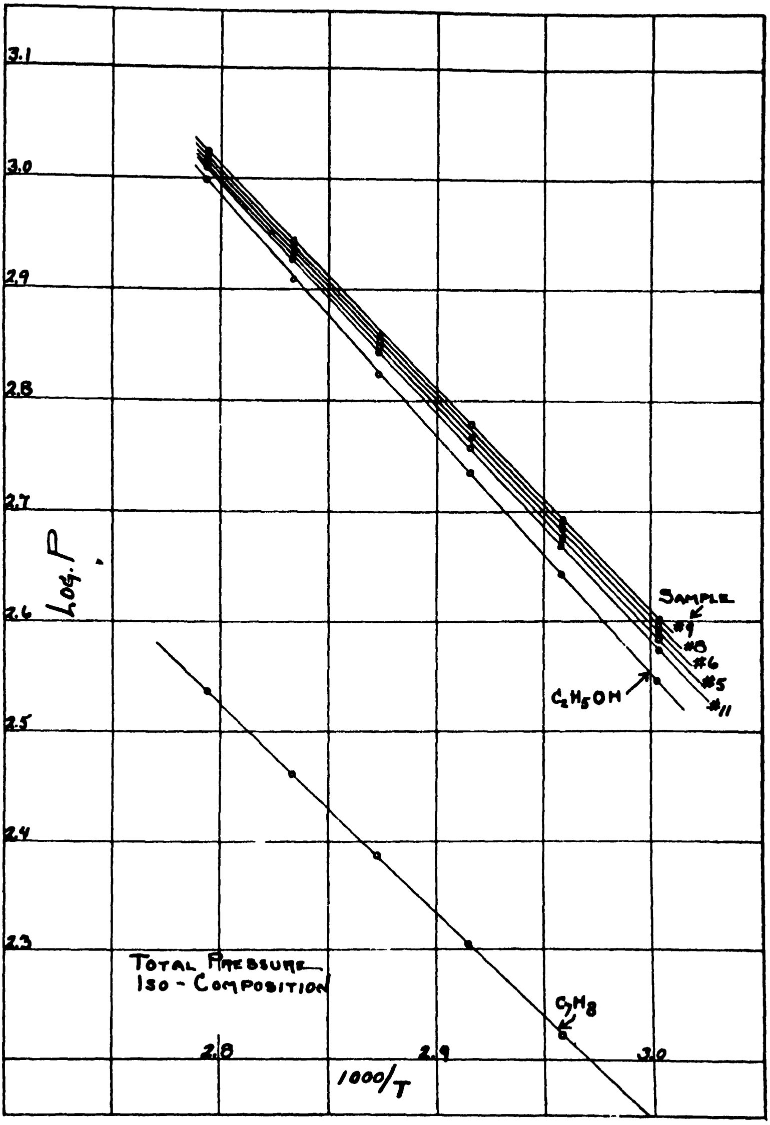

FIG. 4. TOTAL PRESSURE ISO-COMPOSITION

the maximum, or azeotropic point, is shifting so slowly that the temperature at which this would happen would be quite high. Predictions made by the extensions of the straight lines obtained are accurate throughout the range where the pure liquids give a straight line when log P is plotted against $1/T$.

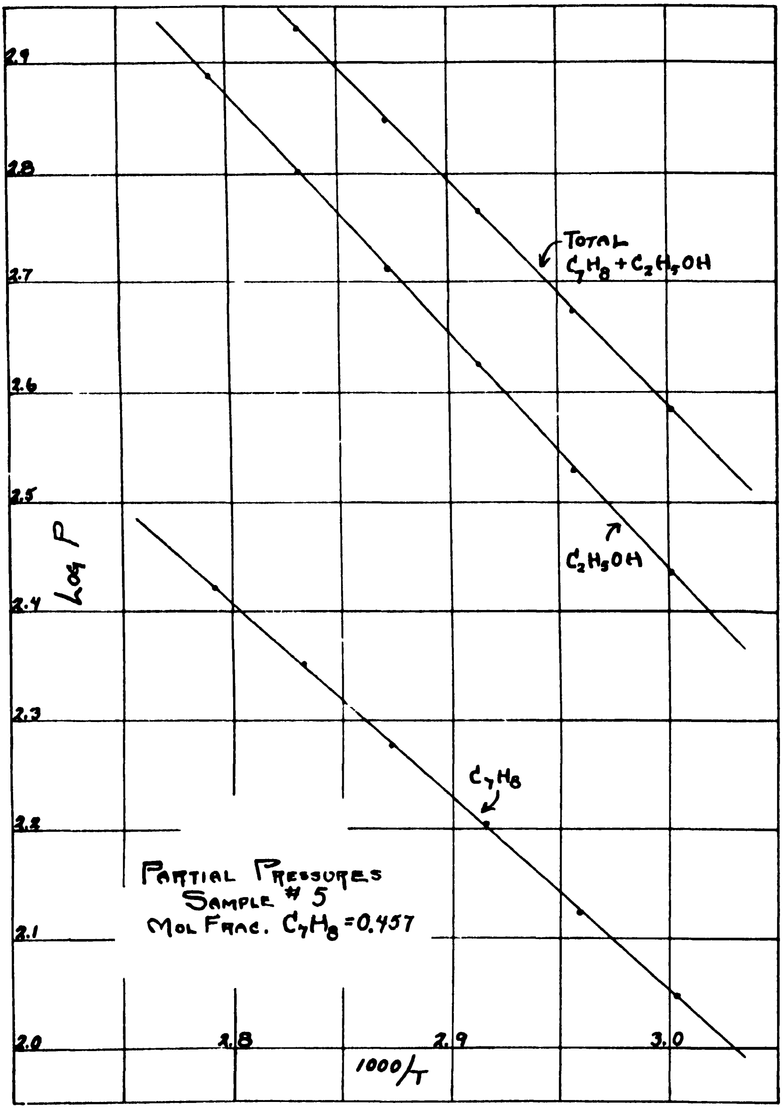

Fig. 5. Partial Pressures
Sample No. 5; mole fraction of toluene = 0.457

A liquid mixture, when outlined as described, becomes a versatile source of data. Aside from the prediction of pressure, temperature, and composition equilibria, graphs of the type of figure 4 have been used to calculate the heats of vaporization at any desired temperature and composition.[2] Similarly, from the graphs of the type of figure 5 the partial heats of vaporization at any particular point were calculated. Studies on activities and activity coefficients can be made, prediction of the shift of the azeotropic point, etc.

SUMMARY

(1) In the study of liquid mixtures, the desirability of data in sufficient quantities to give a matte when plotted is pointed out.

(2) An apparatus is described and the procedure outlined for the determination of such data.

(3) A very complete examination of the system, toluene–ethyl alcohol, has been made over a pressure range of 700 mm. and its attendant temperature changes.

(4) As a consequence of the character of the data obtained, some generalizations are made on the laws of liquid mixtures, permitting equilibria predictions and calculations such as the heat of vaporization or the partial heats of vaporization at any point. The generalizations made in the paper have been tested with data from the literature and further confirmation obtained of their value.

REFERENCES

(1) Swietoslawski: Bull. soc. chim. **50**, 1568 (1931).
(2) Robinson, Wright, and Bennett: J. Phys. Chem. **36**, 658 (1932).
(3) Sameshima: J. Am. Chem. Soc. **40**, 1482, 1503 (1918).
(4) Cunaeus: Z. physik. Chem. **36**, 232 (1901).
(5) Schmidt: Z. physik. Chem **99**, 71 (1921); **121**, 221 (1926)

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[2] These, together with some other similar calculations, may be discussed in a later paper.

DIFFUSION IN STANDARD CELLS

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Our principal standards of electromotive force are: (1) the zinc (Clark) cell, $ZnAm/ZnSO_4 \cdot 7H_2O$, Hg_2SO_4/Hg; (2) the cadmium (saturated) cell, $CdAm/CdSO_4 \cdot 8/3H_2O$, Hg_2SO_4/Hg; and (3) the Weston (unsaturated) cell, $CdAm/CdSO_4$ solution (saturated 4C.)/Hg_2SO_4/Hg. All these cells are built about mercurous sulfate as depolarizer and it is the unique properties of this substance that have made these voltaic combinations useful standards (1). The mercurous sulfate has a solubility of about one gram in a liter in the cathode systems of these cells, while the amalgams of the anode system maintain the concentration of the mercury to something like 10^{-10} gram per liter at the amalgam electrode surfaces (2). Therefore these combinations may be looked on as concentration cells.

It is the function of the mercurous sulfate to maintain a definite concentration of mercury at the mercury cathodes, while the amalgams maintain an equally definite concentration of mercury at the amalgam anodes. These concentrations are widely different so that there must be a continual diffusion of mercury ions from cathode to anode, and this diffusion is an important factor in the slow changes that take place in the E.M.F. of the cadmium and Weston cells (3). It has been shown (4) that neutral cadmium sulfate solutions slowly hydrolyze mercurous sulfate but that the insoluble products of hydrolysis inhibit the reaction, and it is only as these products diffuse away to the anode that the hydrolysis becomes effective, so that it has become of interest to obtain more definite information on diffusion in standard cells.

Properly constructed cells show their normal E.M.F. immediately they are filled, so that the mercurous sulfate promptly establishes its proper concentration at the mercury electrode. The amalgam or anode electrolyte also promptly comes to equilibrium with a definite mercury ion concentration at the anode. The amalgam is able to maintain this concentration even when the mercury ions arrive by diffusion from the cathode, otherwise the arrival of the mercury ions at the anode would be accompanied by a change in the E.M.F. of the cell. The extended observations on zinc cells completely negative this proposition. It seemed of interest to have more information on the diffusion that actually takes place in standard cells. When a cell is freshly filled the electrolyte excepting that in the "paste" is quite free of mercury ions, but the cathode mercury ions begin at once to diffuse toward the anode. The potential of the electrolyte at any point toward a mercury electrode depends on its mercury ion concentration, so that if we determine this potential we have a measure of the mercury ion concentration at the particular point. Now, amalgamated platinum has exactly the same potential as mercury, so we may use a small amalgamated platinum point to explore the electrolyte of cells. We may measure it against the anode or cathode of the cell and so determine the mercury ion concentration at any point in the cells, provided that we know the relation between mercury ion concentrations and potentials in these solutions.

This information we have obtained as follows. A saturated cadmium sulfate solution was rotated at 25.00°C. together with $CdSO_4 \cdot 8/3H_2O$, mercury, and normal electrolytic mercurous sulfate (5) until no further change in concentration took place—two weeks. Two 100-cc. portions of the perfectly clear solution were removed for analysis and to each was added a very slight excess of 0.2 *N* HCl. Under these conditions Hg_2Cl_2 is one of our most insoluble precipitates. In the absence of mercury or a reducing agent the removal of the mercurous mercury does not disturb the mercuric mercury present. Instead of a tared filter paper disk previously employed (6) we used a small-sized Neubauer crucible with a minimum of sponge platinum filtering medium.[1] The Hg_2Cl_2 coagulates, filters, and washes very satisfactorily. The Hg_2Cl_2 is measurably volatile at 100°C. but may be satisfactorily dried in a vacuum desiccator at room temperature and the results are very exact (6). The two determinations checked quite closely, showing 1.122 grams Hg_2Cl_2 from a liter of the saturated $CdSO_4$ solution. This gives a calculated 0.9535 gram of mercurous mercury in one liter, or a concentration of 0.00238 molar.

The filtrates and wash waters were made acid with hydrochloric acid to keep cadmium sulfide in solution and then the mercuric sulfide was precipitated, vacuum desiccated in the Neubauer crucible, and was found to weigh exactly 4 mg. from the 200 cc. of the saturated solution or 0.00354 gram of mercuric mercury from 200 cc. of the saturated solution. This is 0.01725 gram of mercury in one liter, or 0.00086 molar. This indicated a ratio of

$$\frac{\text{Hg(ous)}}{\text{Hg(ic)}} = \frac{0.9535}{0.01725} = 55$$

A portion of the above solution (saturated with $CdSO_4 \cdot 8/3\, H_2O$, Hg_2SO_4, Hg) was brought onto a mercury electrode and joined to a cadmium amalgam–cadmium sulfate half-cell (7). The E.M.F. of this combination at 25.00°C. was 1.019614 volts, confirming previous observations on the rotated cathode system of the cadmium cell (8). Now this voltage of 1.019614 corresponds to a concentration of 0.9535 gram of mercuric mercury and 0.01725 gram of mercuric mercury in a liter of the saturated cadmium sulfate solution at the mercury electrode. By diluting the original solution with known volumes of a saturated $CdSO_4 \cdot 8/3\ H_2O$ solution, we had solutions of known mercury concentration and we observed the potential of each of these on a mercury electrode combined with the cadmium amalgam half-cell. We thus had the cadmium cell combination with known concentrations of mercury at the cathodes. Obviously from E.M.F. values such a table (table 1) gives the mercury concentration at the cathode of any cadmium cell as accurately as we have knowledge of the mercury concentration of our original solution.

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[1] The weight of a large sponge of platinum is not so reproducible on vacuum desiccation, but with our crucible we found the weight reliable to about 0.01 mg.

TABLE 1

SATURATION SOLUTION	Hg_2^{++} PER LITER	Hg^{++} PER LITER	E.M.F. OF CELL AT 25°C
per cent	*grams*	*grams*	
100	0 9535	0 01724	1 019614
95	0 9057	0 01638	1 019050
90	0 8581	0 01552	1 018718
85	0 8104	0 01465	1 018082
80	0 7627	0 01378	1 017593
75	0 7151	0 01293	1 016828
70	0 6674	0 01207	1 018790
65	0 6197	0 01121	1 015093
60	0 0721	0 01035	1 014288
55	0 5244	0 00948	1 013208
50	0 4767	0 00862	1 01160
45	0 429	0 00776	1 010548
40	0 3814	0 00689	1 009058
35	0 3337	0 00603	1 004985
30	0 2860	0 00517	1 002533
25	0 2384	0 00431	1 001543
20	0 1907	0 00343	0 995340
15	0 143	0 00259	0 993793
10	0 09535	0 00172	0 988510
5	0 0477	0 00086	0 993793
4	0 0381	0 00068	0 979933
2	0 0191	0 00034	0 971973
1	0 0095	0 00017	0 962901
0 8	0 0077	0 000136	0 963453
0 6	0 0057	0 000102	0 961043
0 4	0 0038	0 000068	0 955143
0 2	0 0019	0 000034	0 950343

From table 1 it is of interest to note that the cadmium cell with an E.M.F. of 1.01808 volts at 25°C. has a solution next to the mercury electrode which had 0.8104 gram of mercurous mercury and 0.01465 gram of mercuric mercury to the liter. This is only 85 per cent of the concentration obtained by saturating a saturated solution of cadmium sulfate at 25°C. with normal mercurous sulfate in the presence of mercury. Here is further evidence that the cathode systems of our cadmium cells are not equilibrium systems. Indeed it is only necessary to stir the paste of any seasoned cadmium cell (9) to observe a marked increase in E.M.F. followed by a subsequent decrease with the E.M.F. dropping *below* the normal value, which is quite conclusive proof of the instability of this cathode system and confirms the conclusions drawn from the rotation experiments (7).

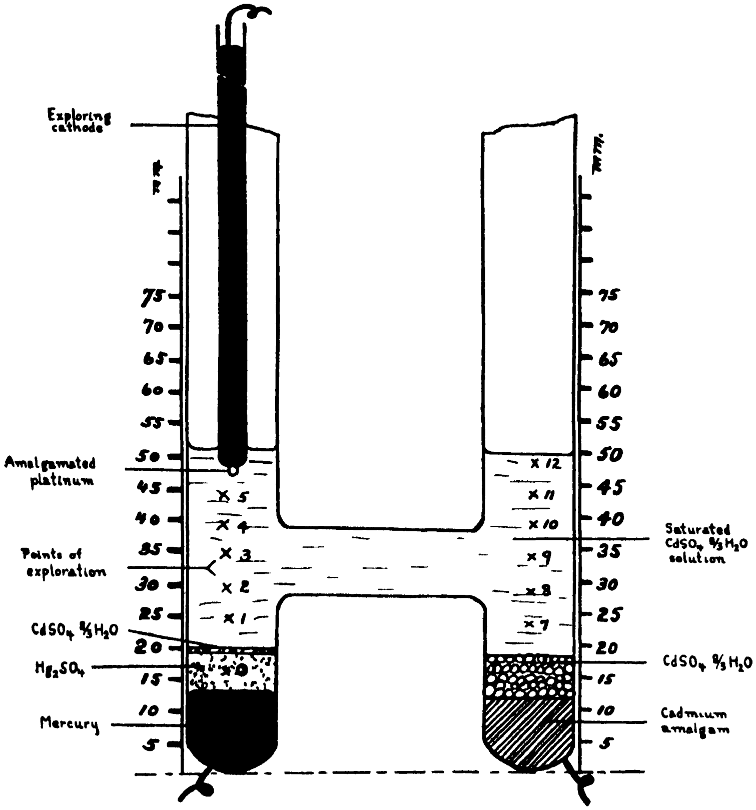

FIG 1

With the information in table 1 we may unseal any cadmium cell and explore the mercury concentration at any point in the electrolyte or paste. Amalgamated platinum has the same potential as mercury. We only need a minute amalgamated platinum point. By placing such an electrode at the desired point in the cell and measuring its potential against the anode from this E.M.F. the table gives the exact concentration of mercurous and mercuric mercury at the point in question. It was of interest now to open cells of different ages and observe how diffusion had progressed. For this purpose two cadmium cells with electrolytic mercurous sulfate as depolarizers made up according to specifications developed in this laboratory were selected (10). One cell, A138, was made in 1914 and the other, G3, was

TABLE 2

LOCUS	E M F	Hg_2	PER CENT NORMAL
		Cell G3	
		mg per liter	
Cell itself	1 018140	817	102
0	1 01791	793	98
1	1 00812	372	45 7
2	1 00697	358	44 2
3	1 00659	354	43 7
4	1 00591	345	42 1
Cathode			
7	1 00437	323	40
8	1 00435	320	39 5
9	1 00431	320	39 5
10	1 00428	320	39 5
		Cell A138	
Cell itself	1 01804	807	99 5
Cathode			
0	1 01727	740	91 3
1	1 01737	745	92 1
2	1 01735	745	92
Anode			
7	1 01738	747	93 15
8	1 01735	745	93
9	1 01735	745	93
10	1 01739	749	93 1

made in 1928. These cells maintained at 25.00°C. were unsealed and the amalgamated point was placed at positions indicated in figure 1. The following observations (table 2) and deductions were made.

It appears that diffusion does not attain a steady state in four years in the cadmium cell, but does inside of eighteen years. There is a distinct concentration gradient in the four year old cell but practically none in the eighteen year old cell. An interesting observation in cell A138 is that the concentration of mercurous mercury in the paste is less than that at the surface of the mercury electrode. This may well be due to the presence of much finely divided mercury in the paste, a factor we will consider in a subsequent article.

The above experiments do not give a very good idea of the rate of diffusion in newly constructed cells when it is a maximum. To get a clearer picture of this region we observed a cell constructed as follows. The usual mercury and 10 per cent cadmium amalgam electrodes were used but no paste or mercurous sulfate or cadmium sulfate was introduced into the cell. Instead, a saturated solution of these salts only was employed. The system ($CdSO_4 \cdot 8/3H_2O$, Hg_2SO_4, Hg, H_2O) was rotated at 25°C. for fourteen days and the clear solution taken to fill the cell. The observations are given in table 3. The cell had the high E.M.F. observed in the rotation experiments. Evidently the cadmium amalgam promptly reduced the mercury ions in its vicinity to the equilibrium concentration. Diffusion to

TABLE 3

TIME	E M F	Hg_2	PER CENT NORMAL
days		*mg per liter*	
0	1 019610	953 45	117 6
1	1 019053	905 72	111 7
2	1 018897	895 0	109 00
6	1 008719		47 0
7	1 005744		38 4
11	1 00120	236	29 1
20	0 99934	222	27 3
36	0 991857	124	15 3
53	0 980871	50	6 15
61	0 964187	9 53	1 08
74	0 956526	7 15	0 88
100	0 946194	2 38	0 29

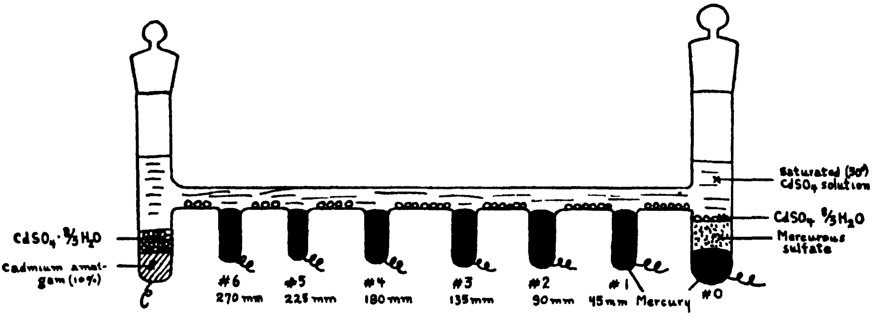

FIG. 2

TABLE 4

CELL		TIME	CATHODE NO 6	CATHODE NO 5	CATHODE NO 4	CATHODE NO 3	CATHODE NO 2	CATHODE NO 1	CATHODE NO 0
Electrolytic Cell A	E M F versus anode	1st day	0 97530	0 98477	0 98574	0 98641	0 98835	0 98890	1 018242
	Per cent normal		2 95	7 55	9 44	10 62	11 80	12 98	102 95
Crystalline Cell B	E M F versus anode	1st day	0 97459	0 98279	0 98829	0 99181	0 99368	0 99493	1 01865
	Per cent normal		3 24	7 67	11 50	15 6	17 65	19 4	109 44
Electrolytic Cell A	E M F versus anode	6th day	0 98442	0 98195	0 99910	0 9940	0 99968	0 99993	1 018157
	Per cent normal		8 55	7 05	26 5	27 1	27 7	28 5	102 06
Crystalline Cell B	E M F versus anode	6th day	0 99852	0 99907	0 99965	0 99982	0 99982	1 00031	1 01849
	Per cent normal		24 6	26 2	26 7	27 6	27 7	28 2	107 1
Electrolytic Cell A	E M F versus anode	65th day	1 00437	1 00438	1 00460	1 00511	1 00566	1 00664	1 01804
	Per cent normal		35 3	35 6	36 2	37 6	38 5	40 5	99 4

the anode began as soon as the cell was filled, and inside of twenty-four hours the diffusion began to affect the cathode potential, resulting in a decreased concentration at the mercury electrode. After six weeks the rate of this drop is pronounced, and in some three months there are exceedingly few mercury ions left about the cathode, so that this cathode potential is approaching the equilibrium value of mercury in saturated cadmium sulfate solution (11).

Further information was sought by observations on some special cadmium cells with a long connecting tube between anode and cathode, 31 cm. long and 10 mm. diameter (figure 2). This connecting tube carried small mercury electrode pockets spaced 45 mm. apart so that it was possible to observe the mercury ion concentrations at these various stations along the cross tube and so the changes with time. One cell was made up with the standard electrolytic mercurous sulfate as depolarizer and the other with our crystalline (12) mercurous sulfate as depolarizer. The electrolyte was saturated at above 25°C., so that it deposited some $CdSO_4 \cdot 8/3H_2O$ crystals along the cross tubes. The table given above gives the relation between E.M.F. and mercury ion concentration at the cathode. At 25°C. a cadmium cell with an E.M.F. of 1.01808 volts has a concentration of 810.43 mg. of mercurous mercury and 14.65 mg. of mercuric mercury to a liter of solution in contact with the mercury electrode. Taking these values as normal we have the observations given in table 4.

It appears from these experiments that the diffusion of mercury ions in standard cells is of considerable magnitude and appears to be greater when the depolarizer is crystalline mercurous sulfate than it is when the electrolytic, precipitate-like product is used for the paste. Evidently the crystalline product is able more rapidly to replenish the ions that diffuse away. When hydrolysis of the mercurous sulfate is possible (4), as in the neutral cadmium or Weston (unsaturated) cells, diffusion may well be an important factor in E.M.F. changes.

REFERENCES

(1) HULETT, G. A.: Trans. Am. Electrochem. Soc. **14**, 65 (1908).
(2) HULETT, G. A., AND DE LURY, RALPH E.: J. Am. Chem. Soc. **30**, 1805 (1908).
(3) HULETT, G. A.: Trans. Am. Electrochem. Soc. **58**, 299 (1930).
(4) GARDINER, W. C., AND HULETT, G. A.: Trans. Am. Electrochem. Soc. **56**, 111 (1929).
(5) HULETT, G. A.: Phys. Rev. **23**, 175 (1906).
(6) HULETT, G. A.: Z. physik. Chem. **49**, 500 (1904).
(7) HULETT, G. A.: Phys. Rev. **23**, 176 (1906).
(8) Reference 7, page 180.
(9) HULETT, G. A.: Phys. Rev. **30**, 652 (1910).
(10) HULETT, G. A.: Phys. Rev. **32**, 257 (1911).
(11) Reference 2, page 1825.
(12) ELLIOTT, R. B., AND HULETT, G. A.: J. Phys. Chem. **36**, 2083 (1932)

SOME HEAT CAPACITY DATA FOR DURENE, PENTAMETHYLBENZENE, STILBENE, AND DIBENZYL

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A "radiation" calorimeter has been described in detail in a recent paper by Thomas and Parks (1). While this calorimeter was developed primarily for the measurement of the specific heats of boron trioxide glass at moderately elevated temperatures, it was later used very successfully in a study (2) of the heat capacities of eleven organic substances between room temperature and about 200°C. Continuing this latter application of the "radiation" calorimeter, we have now obtained specific heat and fusion data for the following four compounds: durene, pentamethylbenzene, stilbene, and dibenzyl.

MATERIALS

Durene and pentamethylbenzene

The samples of these two hydrocarbons were generously presented to us by Professor Lee Irvin Smith of the University of Minnesota. Details concerning them will not be given here, as their preparation and properties have been fully described elsewhere (3). The sharpness of their fusion curves indicated very satisfactory purity.

Stilbene and dibenzyl

These compounds were obtained from the Eastman Kodak Company. Two different samples of each compound were subjected to three or more fractional crystallizations from ethyl alcohol. The melting points of the best products were: stilbene, 124.4°C.; dibenzyl, 51.3°C.

EXPERIMENTAL RESULTS

Table 1 presents specific heat data for the solid and liquid states of the four hydrocarbons investigated. In each case a large number of individual determinations (forty to one hundred) of the specific heats were made. From a plot of these results a smooth curve was then constructed, and from this the values given in the table were taken. In no case were the actual experimental points more than two per cent off this curve. The absolute accuracy of the tabulated mean values is believed to be within two or three per cent.

The literature apparently contains no specific heat values for any of these substances within the temperature range of this investigation. However, our data fit fairly well with the results obtained in this laboratory at lower temperatures by use of the Nernst method with an aneroid calorimeter. Thus, for example, Huffman, Parks, and Barmore (4) report a value of 0.383 calorie per gram for durene at 24.0°C, while the curve for our present data, if extended, would lie about one per cent below this figure.

TABLE 1

Specific heat data for crystals and liquid

TEMPERATURE	DURENE	PENTAMETHYLBENZENE	STILBENE	DIBENZYL
degrees C	*calories per gram*	*calories per gram*	*calories per gram*	*calories per gram*
30	0.384	0.431		0.337
40	0.395	0.443	0.317	0.351
50	0.410	*m.p. 54.3°C*	0.328	*m.p. 51.3°C*
60	0.421	0.457	0.338	0.417
70	0.433	0.464	0.349	0.425
80	*m.p. 78.9°C*	0.471	0.360	
90	0.487	0.478	0.370	
100	0.493	0.485	0.381	
110	0.499	0.494	0.391	
120	0.505	0.504	*m.p. 124.4°C*	
130			0.466	

TABLE 2

Fusion and transition data

SUBSTANCE	NATURE OF CHANGE	TEMPERATURE	HEAT EFFECT
		degrees C	*calories per gram*
Durene	Fusion	78.9	38.0
Pentamethylbenzene	Transition	23.2	2.9
Pentamethylbenzene	Fusion	54.3	19.9
Stilbene	Fusion	124.4	36.9
Dibenzyl	Fusion	51.2	29.6

The four fusion values for these compounds, together with a result for the heat of transition of the pentamethylbenzene in the solid state, are given in table 2. For durene our result is in good agreement with a value (37.5 calories per gram) calculated by Smith and MacDougall (3) from measurements of the freezing points of solutions of isodurene in durene and also with an experimental value (37.98 calories per gram) recently obtained by

Zeumer[1] in Professor Roth's laboratory at Braunschweig. Likewise, our heat of transition of pentamethylbenzene compares favorably with the result (3.19 calories per gram) obtained previously by Huffman, Parks, and Barmore (4) with a Nernst calorimeter which had been designed for low-temperature work. However, our fusion value for stilbene is considerably lower than the 40.0 calories per gram reported by Padoa (5) and our result for dibenzyl is also somewhat lower than the values of Padoa (5) (31.0 calories per gram) and of Bogojawlensky and Winogradow (6) (30.4 calories per gram).

Before concluding, the authors wish to thank Professor George S. Parks (under whose direction the investigation was carried out) and Dr. F. O. Koenig for their interest and advice during the progress of the work.

SUMMARY

Data for the specific heats (in both the solid and liquid states) and the heats of fusion of durene, pentamethylbenzene, stilbene, and dibenzyl have been obtained with a "radiation" calorimeter.

REFERENCES

(1) Thomas and Parks: J. Phys. Chem **35**, 2091 (1931).
(2) Spaght, Thomas, and Parks: J. Phys. Chem. **36**, 882 (1932).
(3) Smith and Lux: J. Am. Chem. Soc. **51**, 2994 (1929).
Smith and MacDougall: J. Am. Chem. Soc. **51**, 3001 (1929).
(4) Huffman, Parks, and Barmore: J. Am. Chem. Soc. **53**, 3880 (1931).
(5) Padoa: Atti accad. Lincei **28**, 239 (1919).
(6) Bogojawlensky and Winogradow: Z. physik. Chem. **64**, 251 (1908).

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[1] Private communication to Professor Parks from Dr. Hans Zeumer. This result was obtained by the use of a method of mixtures.

COMMUNICATIONS TO THE EDITOR

X-RAY STUDIES OF FATTY ACIDS AND OF MIXTURES OF FATTY ACIDS

In view of the time-consuming nature of this work a preliminary report is given at this time.

X-ray studies have been made of samples of the saturated normal fatty acids with ten to eighteen carbon atoms, and the large crystal spacings have been measured with great accuracy. (These samples, which represent the purest acids now available, were prepared by Dr. J. Ruhoff and Dr. J. D. Meyer with Professor E. E. Reid in this laboratory in the course of an investigation which will be published shortly.) In comparison with similar studies (Francis, F., Piper, S. H., and Malkin, T.: Proc. Roy. Soc. **A128**, 214 (1930)) made with the purest acids previously available, we find definite deviations which do, however, not exceed one per cent.

Francis, Piper, and Malkin have made a very interesting study of equimolar mixtures of fatty acids containing n and n + 1 carbon atoms. Their results, expressed as simply as possible, indicate that a characteristic long spacing is obtained for such mixtures and that the spacing is the mean value of the spacings the pure components would have if they crystallized in the same modification (same tilt of the fatty acid molecules, which are parallel to the C-axes of the crystals). Since the building elements of such crystals are double molecules they propose the following explanation. In the case of the mixtures the double molecules are obtained essentially by combination of a long and a short single molecule. This theory did not appeal to us for various reasons. The experimental test is given by a study of mixtures in non-equimolar proportions. In the case of the mixture of C_{10} and C_{11} for instance, we have studied the whole range in ten equal steps. We find the equimolar mixture to be the actual mean of the C_{10} and C_{11} spacings, but any of the other mixtures gives also single, sharp spacings, which follow roughly a linear relation with the composition. Thus, it is obvious that the theory proposed does not hold, but that the phenomenon is analogous to ordinary mixed crystal behavior, the relation being approximately expressed by Vagard's rule.

That our point of view is correct is also indicated by the fact that previous work on various non-equimolar mixtures of C_{16} and C_{18} gives definite spacings varying according to composition between the values of the two components. (Piper, S. H., Malkin, T., and Austin, H. E.: J. Chem. Soc. **1926**, 2310.) In this and other cases for mixtures of n and n + 2 we have found similar results.

For mixtures of the n and n + 3 acids we find, similar to Francis, Piper, and Malkin, mixed-crystal spacings. According to these authors such combination does not occur in mixtures of n and n + 4 acids. This is contrary to our results; the equimolar mixture of C_{14} and C_{18}, for instance, gives the spacing of the C_{16} acid.

For two-component mixtures of acids of still larger differences in chain length we have not been able as yet to obtain appreciable mixed-crystal formation.

It seemed of interest to study mixtures of a large number of components, for it was anticipated that in such cases mixed-crystal formation would be possible over a much wider range. Actually it was found that approximately equimolar mixtures of the acids with n = 11, 13, 15, and 17, n = 10, 12, 14, 16, and 18, and finally a mixture of n = 10, 11, 12, 13, 14, 15, 16, 17, and 18 in each case gave rise only to one definite combination spacing, this value lying between the two corresponding extremes and closer to the higher one.

It seems that these experiments are important for the interpretation of x-ray diagrams of highly polymerized substances. Such bodies are in many cases assumed now to consist of chain-like molecules of varying lengths. Such systems were up to now not expected to yield any x-ray interferences connected with the chain length. Our results seem to indicate that this point of view must be modified. In an earlier paper (Ott, Emil: Z. physik. Chem. **B9**, 378 (1930)) it was shown that definite chain lengths could be assigned to certain polymer formaldehydes. Although the author was at that time inclined to his present outlook, it seemed safer to conclude, in agreement with the prevailing opinion, that the result indicated that such polymers were built up essentially of molecules of a given length only. At present it appears quite reasonable to consider the chain length mentioned as corresponding to an "average" length. This is of course in better agreement with the chemical experience. It is probably for the latter reason that Sauter (Z. physik. Chem. **B18**, 417 (1932)) attacks the view of the author; his evidence, however, is essentially negative. This point shall be tested further in due time. At present it seems to us most essential to increase the knowledge concerning x-ray diffraction of such well-defined systems, which may serve as a model for high polymers. The results thus far obtained in this direction seem to favor our point of view.

These investigations are being continued and with other coworkers extended to other groups of long-chain compounds.

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BINARY SYSTEMS OF *m*-NITROTOLUENE AND *p*-NITROTOLUENE WITH NAPHTHALENE, *p*-TOLUIDINE, AND *o*-NITROPHENOL

In a continuation of the studies of the binary systems of the various nitrotoluenes with a second component which have been carried on in the Department of Chemistry of the University of North Carolina the following systems have been investigated: *m*-nitrotoluene–naphthalene, *m*-nitrotoluene–*p*-toluidine, *m*-nitrotoluene–*o*-nitrophenol, *p*-nitrotoluene–*p*-toluidine, and *p*-nitrotoluene–*o*-nitrophenol. The temperature-composition diagrams were determined by thermal analysis, using a calibrated mercury thermometer as the temperature-recording instrument. No compounds were obtained and the formation of solid solutions could not be detected. In plotting the logarithm of the mole fraction of solvent against the reciprocal of the absolute temperature straight lines were obtained, showing that the systems are ideal in nature. The calculated heats of fusion (accurate to about 2 per cent), the eutectic temperatures, and the eutectic composition in mole per cent are given in the following table.

SOLVENT	SOLUTE	HEAT OF FUSION		EUTECTIC TEMPERATURE	EUTECTIC COMPOSITION (SOLVENT)
		Solvent	Solute		
		calories per mole	*calories per mole*	*degrees C*	
p-Nitrotoluene	*p*-Toluidine	3,970	4,158	15.9	46.5
p-Nitrotoluene	*o*-Nitrophenol	4,044	4,183	16.9	47.5
m-Nitrotoluene	*p*-Toluidine	3,365	4,012	−2.6	65.0
m-Nitrotoluene	*o*-Nitrophenol	3,432	4,133	−1.5	68.0
m-Nitrotoluene	Naphthalene	3,022	4,384	4.8	81.5

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CORRECTIONS

The following corrections should be made in the article "Glass Electrode Determination of Sodium," appearing in This Journal, **35**, 3058 (1931):

Page 3061, first line. For "mols NaOH" read "mols NaCl," and for "NaOH found" read "NaCl found."

Page 3061, second line. For "4%" read "4.0%."

Page 3061. For "Fig. 2" read "Fig. 3," and for "Fig. 3" read "Fig. 1."

Page 3062, eleventh line from the bottom. For "unchanged," read "uncharged."

Page 3063. For "Fig. 1" read "Fig. 2," and for "Fig. 2" read "Fig. 1."

F. Urban.
Alexander Steiner.

NEW BOOKS

Dans le champs solaire. BY PAUL COUDERC. Encyclopédie Gauthiers Villars, 1932.

Written as a companion to the author's *Architecture de l'Univers*, the present volume deals, as the title expresses, with the solar system—a rather ungrateful, banal subject, in the author's opinion, when compared with the newer and wider vistas opened in stellar astronomy. In order to preserve the sense of unity with the previous volume, this one has been written with the guiding principle that the methods as well as the results of astrophysics should be accorded the principal emphasis, while furthermore the relationship between the sun and its planetary system and the stellar universe at large should be clearly realized.

It is natural, therefore, to find that the book differs considerably from most treatises on the same subject, and it is emphatically not a textbook. Some of these deviations render the book only more attractive—at least in the reviewer's opinion, such as the historical introduction, and the rather detailed exposition of the various theories for the origin of the system. Some other features would seem to have just the opposite effect, as, e.g., the unduly emphasized description of the earth and its atmosphere, and the very brief, almost hasty, résumé of the planets and their satellites which are accorded barely as much space as the subsequent description of the nearest stars, the motion of the sun among and with these, and that of the structure and motion of the galaxy as a whole—all of which would seem rather irrelevant in connection with the planetary system. More than one-third of the book is devoted to the sun, while comets and meteors, treated almost as an afterthought, coming *after* the description of the solar neighborhood, have no more than eleven pages allotted to them.

Probably all this is due to the desire already referred to, to treat the subject matter from the point of view of astrophysics, and always in relation to the stellar universe. With these limitations in view one must admit that the author has succeeded very well, for the book is clearly and interestingly written and attractively illustrated. I believe, however, that it is a fair criticism to say that it lacks unity; the various chapters are somewhat disjointed, and give the impression more of separate articles written for different purposes.

As to more specific criticisms: on page 36 one reads that it was *Bowen*, who cleared up the mystery of the *Aurora* line, while on page 81 one obtains the impression that, among others, the Harvard and Victoria Observatories concern themselves "more or less" with solar studies. The illustrations on the sun may well be called superb; several of those portraying lunar phenomena under high magnification, are, however, distinctly mediocre.

W. J. LUYTEN.

Hydrogen Ions. BY F. T. S. BRITTON. 22 x 14 cm.; pp. xvi + 589. London: Chapman and Hall, 1932. Price 25 shillings (not 52 shillings as erroneously printed in the number for October, 1932). For review see volume 36, page 2687.

Treatise on Sedimentation. Second edition. BY WILLIAM H. TWENHOFEL AND COLLABORATORS. pp. 960; 121 text figures: 8 chapters. Baltimore: Williams & Wilkins, 1932. Price: $8.00.

The book is a product of the work of the Committee on Sedimentation of the Division of Geology and Geography of the National Research Council. The first edition was published in 1926. The plan of the second edition follows closely that of of the first. Many specialists submitted manuscripts treating of the phases of sediments and sedimentation most familiar to each of them. These manuscripts were organized and edited by Mr. Twenhofel and incorporated into a single volume. The result is a veritable mine of information on the various phases of sediments and sedimentary rocks. The chief advantage of this edition is that it gives a more complete list of footnote references, especially to foreign literature. The book thus provides in compact form, information that would otherwise require extended bibliographic search. It becomes a logical starting point for any investigation involving sediments and their relationship.

Many subjects of interest to the student of physical chemistry are presented. These include such matters as the stabilization of hydrosols of iron and manganese by organic colloids; colloidal calcium carbonate and its influence in the formation of limestone; the amount and nature of colloidal silica in ground water, streams, lakes and seas, and the various modes of its precipitation; the transportation of matter in the colloidal state; the flocculation of colloids in brackish water and marine environments and the electrolytes instrumental in producing the reaction; the behavior of gels of silicious dioxide, hydrated aluminum oxide, hydrated ferric oxide and humic acid compounds in clayey sediments and soils; the nature and causes of stratification in colloidal sediments; and the colloidal ground-mass of coal.

The reviewer considers this edition a more complete, better organized, and more authoritative contribution than the first edition. It contains few if any of the infelicities of expression, misspellings and typographical errors which marred the earlier volume. It is a compilation that does much to advance an understanding of the many intricate problems confronted by all students of sediments.

GEO. A. THIEL.

Organic Chemistry. BY PERKIN AND KIPPING. Fifth edition, Parts I and II, completely revised and rewritten, by F. Stanley Kipping and F. Barry Kipping. pp. 614 + xxix. Philadelphia: J. B. Lippincott Company, 1932.

This work comprises the first two of the three parts of the latest edition of an old, standard textbook on organic chemistry. In style and format, there is little change, but the subject material has been brought up to date and many of the chapters have been completely rewritten. There are useful summaries at the end of each chapter.

Parts I and II cover the important aliphatic and aromatic compounds and related material, while in part III it is planned to cover various special branches of organic chemistry such as terpenes, cycloparaffins, and the like.

The book is intended for use both as a text and a laboratory manual, but the directions for preparing substances in the laboratory are inserted in the text along with the descriptive matter. On page 614 there is a special index to these laboratory preparations, comprising about eighty laboratory experiments.

The printing is well done, the paper is excellent, and the book is very readable. The index is quite adequate.

LEE IRVIN SMITH.

An Introductory Course in Physical Chemistry. By WORTH E RODEBUSH. 22 x 14 cm.; pp. xiii + 421. New York: D. Van Nostrand Company, 1932. Price: $3.75.

"A generation ago physical chemistry was studied only by a few students who were particularly interested in the subject and who possessed some special aptitude for it. From such a modest beginning, this branch of chemistry has rapidly increased in popularity. During the last decade more than a thousand students have studied physical chemistry at the University of Illinois." Page v.

"The material presented is about the same as will be found in the average course in physical chemistry, although the order is somewhat novel in that chemical equilibrium is taken up early in the course. This is a tremendous advantage from the point of view of logic and involves no difficulty for the student since he has become familiar with reversible reactions in his inorganic chemistry." Page vi.

The headings of the chapters are: the atom and the molecule; the kinetic theory of matter—gases; the kinetic theory of matter—liquids; the crystalline state of matter; laws of chemical equilibrium; equilibrium between different phases of a pure substance; solutions; surface chemistry ana solutions; equilibria involving ions in solution; conductivity; electrode potentials; the concept of entropy and the third law of thermodynamics; physical properties and molecular constitution; the rate and mechanism of chemical reaction; the atom; the molecule; the activation of atoms and molecules.

The reviewer approves highly of treating equilibrium before reaction velocity. It is the only rational way to do things because there is or should be a relation between the stoichiometrical and mass law equations, whereas the reaction velocity equations do not necessarily tie up with much of anything.

There are a number of other good things in the book. "There are certain rules governing the formation of mixed crystals. The substances must be of similar structure chemically. They must be isomorphous; that is, they must have the same crystal structure. The dimensions of the two lattices must be nearly the same. Sodium chloride and potassium chloride do not, to an appreciable extent, form mixed crystals at 25°C. because they do not satisfy the last condition. For miscibility in any proportion the difference between the dimensions of the two lattices can not exceed a few per cent. The tolerance is greater near the melting point." Page 74.

"In this chapter we have learned that chemical reactions do not take place between stable molecules, but between excited molecules, between fugitive aggregates such as hydroxyl, and often between atoms. For lack of a better term, we may characterize this branch of chemistry as the chemistry of the atom. It is still a comparatively unknown subject. We do not know very much about the chemical properties or reactions of the atoms. For example, atomic hydrogen may act as an oxidizing agent and atomic oxygen may act as a reducing agent. It is evident that the chemistry of the future will be very much the chemistry of the atom." Page 340.

"The metallic lattice is of the atomic type. Carbon forms an atomic crystal in diamond but diamond is not metallic in character. It is evident that one of the distinguishing characteristics of the metallic lattice is that it is primarily not a valence type of crystal. In general the atom in a metallic lattice is surrounded by too many other atoms for valences to have much significance." Page 398.

"It is of course rather naïve to suppose that any complicated set of phenomena in nature can be described exactly by a simple mathematical formula. Since van der Waals, literally hundreds of equations of state (any equation which gives the relation between pressure, volume, and temperature for any given mass of a substance is called an equation of state) have been proposed. Some of these are useful for specific cases but in general all are simply empirical formulas which fit the better the more adjustable constants they contain." Page 26

"The summation of the quotients obtained by dividing each quantity of heat by the absolute temperature at which it was absorbed depends only upon the states of the system before and after the change and is independent of the path by which the change takes place. This is an experimental generalization that is just as important as that underlying the first law." Page 103.

The authors are a bit pessimistic over physical chemistry as chemistry. "As a matter of fact the 'normal' type of liquid consists chiefly of the common organic liquids with boiling points a little above room temperature, which are available in large numbers for experiment. One suspects that that is the reason they are called normal liquids." Page 55.

"Everything said so far has referred to association in the vapor phase. We know very little about association in the liquid phase, although some authors have attempted to explain all deviations from ideal solution by association. Solvents such as benzene are sometimes termed *associating solvents* on the theory that solutes have a tendency to polymerize in these solvents, but there is no evidence to support this view. In fact as we have been at great pains to point out, we have no means of determining the state of polymerization of solute or solvent in solution." Page 161.

"It is a tradition in physical chemistry textbooks that some space must be devoted to osmotic pressure, although osmotic phenomena are of much greater interest to the physiologist than to the chemist." Page 168

"The typical strong electrolytes have certain characteristic physical properties such as high melting point and electrical conductivity in the pure liquid state. Hydrogen chloride is a gas at 25°C. and when condensed to a liquid at low temperatures it shows no conductivity; yet it is a typical strong electrolyte in solution. The explanation for this is that an ionized salt $H_3O^+ Cl^-$ analogous to $NH_4^+ Cl^-$ is formed in solution." Page 188.

"In order to simplify the notation and get around the difficulty of the various unknown factors which are involved in dealing with equilibria involving ions, G. N. Lewis invented the concept of activity. The activity of an ion is defined as the total molality of the ion multiplied by an experimentally determined correction factor, the activity coefficient. By the 'total molality' of an ion we mean the molality calculated on the assumption that all electrolytes present in solution which contain the ion are completely dissociated. The activity of an ion, e.g., Cl^-, is represented by the symbol $[Cl\ ]$ and the activity coefficient will be represented by γ. The relation is then:

$$[\mathrm{Cl}\ ] = \gamma_{\mathrm{Cl}^-} m_{\mathrm{Cl}^-}$$

The activities are of course the effective concentrations which we shall use in the expression for the equilibrium constant of a reversible reaction involving ions.

"The student may wonder what is to be gained by the use of empirical correction factors to make a mathematical relation true. The justification is that of utility. If we have values of γ conveniently tabulated we can make accurate calculations of the equilibria where ions are involved." Page 193.

"When the concept of activity coefficient was introduced at the beginning of this chapter, it was expressly stated that only the mean activity coefficient for a pair of ions may be determined experimentally. This point needs to be recalled in connection with the foregoing discussion of hydrogen-ion activity. Regardless of the method used for the determination of hydrogen-ion 'concentration' the only thing that can be determined directly is the mean activity of the hydrogen-ion and associated anion. Any estimate of the individual activity of the hydrogen-ion involves assumptions." Page 218.

"It has been proposed to determine the true transference number by adding a non-electrolytic substance as a reference solute. The reference solute is assumed to remain stationary and from its concentration at the end of the run the difference in the amount of water transferred by the two ions may be calculated. The assumption that the reference solute remains stationary is very probably not justified. In dilute solution the transfer of water causes a negligible error in the transference number." Page 240.

"If a gradually increasing voltage is applied to a pair of inert electrodes in solution and the current plotted against voltage we obtain a curve such as is shown in figure 77 It has often been supposed that if the straight part of the curve were extrapolated back to zero current the corresponding voltage would be the 'decomposition potential ' There seems to be no particular significance to this voltage, however " Page 273

"A fast dye is a contradiction in terms " Page 289 "It has been known for a long time that photographic plates could be sensitized to green and red light by certain dyes The exact mechanism of this photosensitization is not known with certainty Since fluorescent dyes do not show this effect especially, it seems that the mechanism is not one in which radiation is re-emitted by the sensitizing agent " Page 339

"As we have learned more about the behavior of the atom we have been forced to the inevitable conclusion that the energy that is associated with lights exists in corpuscles that we call photons The number of photons in the beam is proportional to the intensity If we know the original intensity of the beam and the characteristics of the grating we can calculate by the wave theory the intensity in the diffracted beam, but all we shall ever observe in the diffracted beam is the number of photons transmitted per second Now if no medium exists for the transmission of light waves and we never observe these waves directly, the question arises naturally as to whether these waves really exist This is a question, however, for the philosopher rather than the scientist So far as the scientist is concerned, the electromagnetic theory of light is a mathematical theory which describes the behavior of light if one assumes a simple relation between the number of photons and the square of the amplitude of the wave, but the thing really observed is the number of photons " Page 335

The reviewer doubts whether the student will grasp the fact that the 2 in the phase rule equation refers to pressure and temperature, page 126 The paragraph on flotation, page 185, is surprisingly obscure On page 249 the authors prove that there is no potential difference between two metals This is proving too much because there would then be no thermopiles Cannizzaro's name is spelled wrongly on page 4

"Pure water will dissolve a considerable amount of ether If sodium chloride is added to the solution the ether will separate out as a second layer This 'salting out effect' is easily explained in terms of dielectric constant An electrical charge attracts a medium of high dielectric constant in the same way that a magnet attracts material of high permeability, e g , iron Since the dielectric constant of water is so much greater than that of ether, the water is pulled into the field existing between the ions and the ether is thrown out " Page 296

This explanation does not seem to harmonize with the fact that if one added alcohol to a saturated sodium chloride solution, some of the salt is thrown out The dielectric constant cannot always be on the job

WILDER D BANCROFT

Recent Advances in Atomic Physics By GAETANO CASTELFRANCHI Translated by W S Stiles and J W T Walsh Vols I and II 20 x 13 cm , pp Vol I xii + 372, Vol II xii + 412 Philadelphia P Blakiston's Son and Co , 1932 Price $4 00 each volume

This is a translation of the third Italian edition with omission of the chapters on Brownian movement, relativity and mass, and astrophysics In the first volume, which deals with atoms, molecules, and electrons, the chapters are entitled atoms and molecules in physical chemistry, light, the kinetic theory of gases, fluctuations; electrons and positive rays, isotopes, x-rays and the atomic number, crystals;

radioactivity; the atomic nucleus. In the second volume, which deals with quantum theory, the headings are: thermal radiation and quantum theory; spectroscopy, Bohr's theory and the energy levels of the atom; Stark and Zeeman effects—multiplet lines—the spinning electron; specific heats; the photoelectric effect—the reverse effect—photoelectric cells and their applications; the Compton effect—light quants; magnetism and the quantum theory; wave mechanics and quantum mechanics—applications; the new statistics—applications.

"The spherical electron, with the radius assumed above, is a pure supposition based on the hypothesis originally made; at present, however, it seems less necessary to consider the spherical electron with a fixed radius, since modern tendencies seem to lead to the conclusion—as we shall see in what follows—that the electromagnetic theory is no longer applicable to systems of atomic dimensions and therefore still less to electrons which are constituent parts of atoms; the structure of the electron is certainly one of the mysteries of contemporary physics " Volume I, page 146.

From Sommerfeld's theory one can deduce that "the ratio of the thermal to the electrical conductivity of a metal is independent of the nature of the metal and is proportional to the absolute temperature." Volume I, page 178.

"Thus, after the lapse of some years, the old hypothesis proposed by Prout at the beginning of the nineteenth century, viz , that the different elements are composed of a single primordial material, has been restored once more to a place of honour; thus science, through a new discovery, and by a road quite different from that followed for several decades, has found—and not for the first time—the confirmation of an idea which was originally put forward solely as a reasonable hypothesis." Volume I, page 203.

"Let us take a milligram of radium and observe its transformation. Why does one atom suddenly explode and die, why does another atom live for a day, another for a week, others for a month, a year, a century? If atoms are all alike, how is it that they are 'healthy' and 'unhealthy' ones? At the present time physics is unable to provide an answer to this question.

"However, since every fact is connected with some other, from which it results, by the chain of cause and effect, according to our rational line of thought (*determination*) we are led to think that, in reality, there must be a complex universe in every atom, and, by reason of the intervention of causes not known to us, the death of an atom is occasioned from time to time. Exactly similarly, in considering the incidence of mortality in a city, we cannot know *which individuals* will die on the morrow, but we can know *how many*, because the mathematics of probability has shown us how we may overcome our ignorance, our inability to take account of the extraordinary complication of elementary causes. We are here confronted with a practical problem which is insoluble, though perhaps not for ever." Volume I, page 302.

"Planck's bold hypothesis, deduced by an involved process of reasoning from statistics and thermodynamics, received very careful consideration at the hands of the more enlightened physicists, the more profound thinkers of the time; nevertheless in spite of the support of men like Einstein and Poincaré, it would probably have been relegated to the philosophy of physics and buried for all practical purposes, if certain experimenters had not been led to examine other phenomena, more simple and less abstruse, which indicated the existence of a discontinuity in nature which, until then, had been entirely unsuspected. While Planck in 1900 had simply asserted that the electrons emitted and absorbed energy in fixed finite quantities and shortly afterwards revised this new conception by restricting it to the process of emission, Einstein, in 1905, daringly proposed the theory that these fixed and finite quantities of radiant energy retained their separate identities throughout their journey from the instant of emission to the instant of absorption. In chapter VI we shall examine this reasoning, but for the present we shall confine ourselves to mentioning the fact that the latest developments of physics have confirmed the idea that in all *elementary* phenomena, i.e., those which concern a single atom, a single molecule, or a single electron, the discontinuity postulated by Planck is found to exist; in such elementary phenomena Nature proceeds by jumps or degrees; in macroscopic phenomena this discontinuity is hidden and it remained unsuspected by physicists for centuries." Volume II, page 28.

"Niels Bohr, with whose work we shall, in the main, be concerned in this chapter, is not one of those specialists who multiply experiments in a small field without regard to the close relations between the different branches of science. He possesses in high degree the research spirit, coupled with a mental audacity which has enabled him to throw off the old methods and worn-out conceptions, to find new approaches to a higher and more general view of phenomena The experimental facts themselves are of course indispensable to the progress of science. They may in fact be regarded as the bony skeleton which resists the test of time. But, in the face of the mass and variety of observed phenomena, the intelligence would be overwhelmed and science would crack under the weight of material if it were not for the appearance from time to time, of a bold innovator with the theory which will harmonize and regroup the facts of experiment and predict new phenomena." Volume II, page 32.

"When a gas is irradiated with light of frequency greater than the resonance frequency, the return of the atom from the excited state to the normal may occur in stages. This is the phenomenon of fluorescence." Volume II, page 99.

"At low temperatures the atomic heat of solid substance is proportional to the cube of the absolute temperature, a result which Schrodinger has verified conclusively for various substances in a temperature range extending from 20° to 50° absolute." Volume II, page 153.

"Compton observed that, when a beam of X-rays fell on a body, the frequency of the scattered radiation remained unaltered in the direction of the incident rays, but became lower in other directions and depended on the angle of deviation." Volume II, page 196.

"If the luminous intensity is very high, the electromagnetic theory provides a means for calculating exactly both the luminous intensity at different points in space, and the variations produced by the superposition of the waves, variations which agree with those calculated directly from Planck's formula which, in its turn, is based upon and is in accordance with experiment. In the case of very low intensities, however, the formula giving the variations indicates that radiation must be regarded as composed of a collection of discrete particles, but nevertheless the electromagnetic theory—although of a kind which seems quite alien to the problem—enables the distribution of the light quants to be determined whether they be numerous or few. If, *then, we abandon any attempt to determine the path of a single light quant* between the moment and the place of its emission, and the moment and place at which it arrives at the measuring apparatus (the sensitive plate), the electromagnetic theory provides us with the means for determining *the average number of light quants* which reach a given point of an optical system however complicated. The luminous intensity, then, is simply the probable distribution of the photons." Volume II, page 222.

"It appears at first sight, therefore, that the observed magnetic moments should be multiples of the Bohr magneton. In reality they are much more complex, because the atom, in addition to the magnetic moment due to the orbital motion of the electrons, possesses also another magnetic moment which is the resultant of moments associated with the electrons themselves. We shall see, however, that the magneton theory is in fact valid and the magneton is obtained experimentally with the value just calculated." Volume II, page 245.

"Whilst de Broglie and Schrödinger had tried to discover the laws of atomic phenomena in the light of classical methods, and to bridge the gap separating the quantum mechanics of atoms from classical physics, Heisenberg—a few months before the appearance of Schrödinger's first paper—started out from the opposite idea. He considered that only a definite renunciation of the deeply-rooted classical representation could lead to a proper understanding of the *régime* obtaining in the atom. He was convinced that, as a fundamental principle in atomic physics, any attempt at *explanation* was pointless and without meaning, and that all magnitudes not susceptible to direct observation should be excluded from atomic theory." Volume II, page 314.

"One of the fundamental characteristics of the history of Science in recent years has been, strangely enough, to show that every explanation founded on the classical mechanics is quite untenable throughout the whole range of electricity, magnetism and optics, which latter has been proved by Maxwell and Hertz to be a branch of electromagnetism.

"The process of unification, although checked by this discovery, has not been entirely destroyed, but it has had to proceed in the opposite direction; relativity showed that it was not the simplest phenomena of mechanics (those that were studied and classified first of all) which were the most fundamental in character; after Einstein's genius had elucidated matters the opposite was seen to be the case: electrical and magnetic phenomena are the simplest and these lead to a mechanics which is more precise and more complete than the old mechanics.

"Another new and unexpected development of recent years is the discovery of discontinuity in every branch of atomic physics; it is the mysterious law of quanta which reigns supreme, and the discontinuity of atomic phenomena lies at the root of optics, electricity, magnetism and heat; Planck's constant, appearing as it does in the most diverse phenomena, has brought out new connections between different branches of physics. Through Heisenberg's principle it shows what is the region of error, of inaccuracy inevitable in human observation, when we are investigating atomic phenomena." Volume II, page 393

WILDER D. BANCROFT.

Neure Forschungen über die optische Aktivität chemischer Moleküle. By G. KORTÜM. 25 cm. x 16 cm.; pp. 118. Stuttgart: Ferdinand Enke, 1932. Price: R.M. 11.10.

After more than a century of effort, the physical theory of optical rotation is still in the melting-pot. The fundamental basis for this theory was provided in 1824, when Fresnel showed that the optical rotatory power of media such as quartz or turpentine could be explained by postulating that the velocity of transmission of circularly-polarized light in the medium was not the same for circular polarizations of opposite signs. The unequal refraction of *right* and *left* circularly-polarized light, which results from these unequal velocities, was detected by direct measurements with a quartz prism of wide angle, compensated by two prisms of glass; and it is now a well-established practice that, in constructing optical apparatus, *d* and *l* quartz prisms must be used in pairs, in order to avoid the double images which would be produced if the circular double refraction were not compensated in this way.

The influence on optical rotatory power of variations in the wave-length of the light was investigated in the earliest experiments of Biot, who propounded an inverse square law, $a = k/\lambda^2$ as long ago as 1818. A theoretical foundation for these observations was, however, not provided until 1898, when Drude invented a model in which the electrons in an asymmetric medium were assumed to vibrate in spiral instead of linear paths. On this basis he deduced his well-known equation, $a = \sigma k_n/(\lambda^2 - \lambda_n^2)$, where λ_n is a wave-length corresponding to one of the natural periods of the vibrating electron, and k_n is a constant which expresses the magnitude of the partial rotation thereby produced. This equation was checked by a comparison with the data for quartz; but the study of rotatory dispersion had fallen so completely into abeyance (as a sequel to the introduction of the sodium flame as an easy source of monochromatic light) that no data at all were available whereby the validity of the formula could be tested in the case of any of the thousands of optically-active organic compounds in which chemists had demonstrated the existence of optical rotatory power. It was this gap that the reviewer set out to fill by a series of studies of rotatory dispersion which have been in progress during the past twenty years. As a result it has been proved that Drude's formula expresses the rotatory dispersion of a large range of organic compounds with perfect accuracy over the range of wave-lengths to which they are transparent, and that anomalous rotatory dispersions can be represented with the same precision as normal rotatory dispersions, by making use of two terms of opposite sign.

In order to express the rotatory dispersion of a medium in the region of absorption, Drude in 1906 reintroduced a "damping factor" which he had omitted in the simplified equation cited above. He thus provided a theoretical basis for the well-known Cotton effect, which had been discovered in 1896, namely an unequal absorption of *d* and *l* circularly polarized light, which Cotton described as "circular dichroism," and a loop in the curve of rotatory dispersion within the same range of wave-lengths. More recently, Dr. Werner Kuhn, following up the work of Born and Oseen, has shown that a similar pair of equations can be deduced from a model in which optical rotatory power is attributed to an unsymmetrical coupling of electrons, such that when one electron moves in a north-and-south direction the other moves east-and-west. These equations, however, do not represent the real form of the experimental absorption curves, nor of the curves of circular dichroism and of rotatory dispersion in the region of absorption. A "damping factor" that can be used to interpret the effect of "forced vibrations" over a narrow range of frequencies, could in fact scarcely be expected to cover an absorption extending over a range of perhaps 1000 Å.

This difficulty was surmounted in 1915 by Bruhat, who obtained an approximation to the real form of the absorption-curve for carbon disulfide by combining *five* components of the "damped vibration" type, and was thus able to deduce the form of the curve of refractive dispersion in the region covered by the absorption band. By a similar process, Kuhn has deduced an equation for the rotatory dispersion produced by an active absorption band of a form which corresponds with a probability-distribution of frequencies in the band. This equation has been checked against his own experimental data; but, since absorption bands which are steeper on the side of shorter wave-lengths are so uncommon that the reviewer cannot recall any example of this type in a long experience of the absorption spectra of organic compounds, it is unlikely that an equation based on this type of absorption can represent the final goal in the investigations of rotatory dispersion.

The two models cited above lead to an identical numerical relationship between circular dichroism and rotatory dispersion in the region of absorption. Kuhn's equations, however, make it possible also to deduce numerical values for the distance between the coupled electrons, which are generally larger (and some times grotesquely larger) than the extreme diameter of the optically-active molecule. There can, indeed, be little doubt that both models are merely provisional, and are likely to be superseded in the near future by a wave-model which will provide a more realistic basis for the same equations. The present position, is, however, so interesting that there is a widespread demand for an expression in clear and simple terms of the fundamental principles involved in the theory of optical rotatory power. For this purpose the monograph now under review is altogether excellent, since the essential points are lucidly discussed, without introducing unessential equations, which would merely repel or confuse the non-mathematical reader. The monograph is indeed an almost ideal example of the way in which physical theory should be presented to chemical readers, and recalls the masterly way in which under similar conditions the greater physicists (it would be invidious to mention their names) are able to leave their tools in the workshop and display their finished work in clear and vivid outline to a lay audience.

In addition to the physical theory of optical rotatory power, the monograph gives an account of the way in which this property can be correlated with molecular structure and with other physical properties of the molecule, such as its dipole moment, its molecular refraction, and the dissociation constants of the acids used in preparing derivatives of a parent-substance. Here again, it is impossible to praise too highly the thoroughness with which the author has searched the original literature and reviewed impartially the many important contributions that have been made to the subject, especially since the modern period was initiated some thirty-six years ago, by the pioneer work of Drude and of Cotton on the physical side and of Pope on the chemical side. The bibliography of 234 entries will in fact be too useful to be overlooked by subsequent writers on this subject, and evidence of its usefulness as a guide to the literature is provided by the fact that two misprinted references from an earlier version of the bibliography have already been cited in a larger work on the same subject. The monograph may therefore be commended without reserve as an authoritative review of the present position of the fascinating topic with which it deals.

T. M. LOWRY.

THE RÔLE OF FINELY DIVIDED MERCURY IN THE DEPOLARIZER OF THE STANDARD CELL

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THEORETICAL CONSIDERATIONS

Let us consider individually the chemical reactions capable of occurring at the cathode of a standard cell, in which both the mercurous and mercuric ions are present, and their corresponding E. M. F.'s:

$$\text{(a) } 2\text{Hg} = \text{Hg}_2^{++} + 2\text{E};\ \text{E.M.F.} = 0.75 + \frac{RT}{2F}\log(\text{Hg}_2^{++});\ \text{E}_0 = 0.75 \text{ volt}$$

$$\text{(b) } \text{Hg} = \text{Hg}^{++} + 2\text{E};\ \text{E.M.F.} = 0.86 + \frac{RT}{2F}\log(\text{Hg}^{++});\ \text{E}_0 = 0.86 \text{ volt}$$

$$\text{(c) } \text{Hg}_2^{++} = 2\text{Hg}^{++} + 2\text{E};\ \text{E.M.F.} = 0.91 + \frac{RT}{2F}\log\frac{(\text{Hg}^{++})^2}{\text{Hg}_2^{++}};\ \text{E}_0 = 0.91 \text{ volt}$$

The value of the E.M.F. in all these cases is of necessity the same in the cathode limb of the cell but it does not necessarily follow that equilibrium prevails between all the ion species and the mercury. As we ordinarily consider the standard cell we assume that the cathode potential is governed by a very definite concentration of mercurous ions above the mercury surface. However it is far more complicated than this. We have seen (1) that if electrolytic mercurous sulfate is brought to equilibrium at 25°C. in a saturated cadmium sulfate solution in which mercury is present in large globules, the equilibriated solution contains a definite amount of mercurous and mercuric ion in the ratio

$$\frac{\text{Hg(ous)}}{\text{Hg(ic)}} = 55.3$$

Barring supersaturation it would be these concentrations of Hg_2^{++} and Hg^{++} which cause the standard cell as we know it to have its given voltage.

Let us digress a moment on the influence of the various mercury ion concentrations found experimentally (1) on the cathode potential. Normal catholyte contains 0.81043 gram of mercurous ion and 0.01465 gram of mercuric ion per liter, the normalities being respectively $N_{Hg^+} = 0.00404$ (as Hg^{++}, $N_{Hg_2^{++}} = 0.00202$) and $N_{Hg^{++}} = 0.00007303$. The former value is very accurate. If we substitute these values in the above equations we obtain

(a) for the mercury-mercurous potential:

$$\text{E.M.F.} = 0.75 + \frac{0.05915}{2} \log (0.00202)$$
$$= 0.75 + 0.0296\ (-2.69465)$$
$$= 0.75 - 0.0765$$
$$= 0.720 \text{ volt}$$

(b) for the mercury-mercuric potential:

$$\text{E.M.F.} = 0.86 + \frac{0.05915}{2} \log (0.00007307)$$
$$= 0.86 + 0.0296\ (-4.13694)$$
$$= 0.86 - 0.122$$
$$= 0.74 \text{ volt}$$

(c) for the mercurous-mercuric potential:[1]

$$\text{E.M.F.} = 0.91 + \frac{0.05915}{2} \log \frac{(0.00007307)^2}{(0.00202)}$$
$$= 0.91 + 0.0296\ ((-4.13649)\ 2 - 2.69465)$$
$$= 0.91 + 0.0296\ (-5.58233)$$
$$= 0.91 - 0.1645$$
$$= 0.745 \text{ volt}$$

For the present considerations let us consider that the normal electrode potential in (a) is correct. Since we know the exact concentration of Hg_2^{++} by experiment the electrode potential 0.7205 volt must be correct, and for equilibrium to prevail the potential in (b) and (c) must also be 0.7205 volt. Consequently we can substitute this value back into equation b,

$$\text{E.M.F.} = E_0 + \frac{0.05915}{2} \log (N_{Hg^{++}})$$

and determine the normality $N_{Hg^{++}}$.

$$0.7205 = 0.86 + 0.0296 \log (Hg^{++})$$

$$-\ 0.1395 = 0.0296 \log N_{Hg^{++}}$$

$$\log N_{Hg^{++}} = -\frac{(0.1395)}{(0.0295)}$$

$$\log N_{Hg^{++}} = -\ 4.73 = 5.27 - 10$$

$$N_{Hg^{++}} = 1.862 \times 10^{-5}$$

Therefore from these theoretical considerations the ratio of Hg(ous): Hg(ic) would have to be, for equilibrium,

$$\frac{N_{Hg^{+}}}{N_{Hg^{++}}} = \frac{4.039 \times 10^{-3}}{1.862 \times 10^{-5}} = 216.7 \text{ (not divalent} Hg_2^{++})$$

---

[1] The above normal electrode potentials have been taken from No. 8 of Der Abhandlung der deutschen Bunsengesellschaft, calculated presumably from thermochemical and free energy relations.

If the E_0 values are correct in all the above equations, the substitution of the adduced ratio $\frac{(Hg_2^{++})}{(Hg^{++})^2}$ in (c) above should give also the value 0.7205 volt.

$$
\begin{aligned}
\text{E.M.F.} &= 0.91 + \frac{0.05915}{2} \log \frac{(1.862 \times 10^{-5})^2}{(2.02 \times 10^{-5})} \\
&= 0.91 + 0.0296\,((-4.73002)\,2 - 2.69465) \\
&= 0.91 + 0.0296\,(9.46004 - 2.69465) \\
&= 0.91 - 0.1995 \\
&= 0.7105 \text{ volt}
\end{aligned}
$$

This value is in quite good agreement with that which we should expect from the afore deduced concentration of mercuric ions. These calculations nicely corroborate the theory of the diatomic mercurous ion, Hg^+—Hg^+.

Now the cathode potential in the standard cell will be governed by the highest of the three E.M.F. values calculated in (a), (b), and (c) preceding. To determine the relative importance of variations in concentration of mercurous and mercuric ions in the cathode let us inspect each equation separately. If the mercurous ion concentration changes tenfold either way, i.e., from 0.0040397 N to 0.040397 N or 0.00040397 N, the corresponding change in potential calculated from equation a would be $\pm \frac{0.05915}{2} \log 5.0$, since

$$
(\tfrac{1}{2}N_{Hg^+} = N_{Hg_2^{++}}) \text{ or } \pm 0.0296\,(0.69897) = \pm 0.023 \text{ volt}
$$

and its corresponding effect on the E.M.F. of (c) would be even less. Anyhow, a tenfold change in the mercurous ion concentration is quite impossible in view of the slight solubility of Hg_2SO_4. (A maximum increase in the Hg(ous) concentration to 117.6 per cent of its normal value has been recorded (1). If, however the mercuric ion concentration is changed tenfold either way, i.e., from 0.00007307 N to 0.0007307 N or 0.000007307 N (this is very possible in view of the high solubility of $HgSO_4$), the corresponding change in potential, calculated from equation b, would be

$$
\pm \frac{0.0591}{2} \log \frac{(10)^2}{C} = 0.0296\,(1 \times 2) = \pm 0.05915 \text{ volt}
$$

giving this effect preponderance over all others. Furthermore, any gain in the concentration of the mercuric ion would likely be at the expense of the concentration of the mercurous ion and a tenfold increase in the former would have an even greater effect on the ratio $\frac{(Hg^{++})^2}{(Hg_2^{++})}$ than $\frac{10^2}{1}$, and therefore on the electrode potential than 0.05915 volt.

EXPLORATION OF OLD CELLS BUILT UNDER OXIDIZING AND ANTI-OXIDIZING CONDITIONS

In 1928, cells were constructed by Dr. W. C. Gardiner (2), the contents of some of which were saturated with hydrogen and others of which were saturated with oxygen. The purpose of the cells was to determine whether or not the atmosphere oxidized the mercurous sulfate and changed the cell values. Two representative cells were carefully opened and the E.M.F. was explored at various points in the electrolyte by means of an amalgamated electrode (1). The cells showed only the usual concentraton-gradient of mercurous ion, the E.M.F.'s being practically identical through both solutions. If atmospheric oxidation were a factor the the E.M.F. throughout the solution saturated with oxygen would certainly be much greater than that throughout the solution saturated with hydrogen, owing to the greater Hg(ic):Hg(ous) ratio in the first one.

BEHAVIOR OF CELLS WITH FINELY DIVIDED MERCURY PRESENT

Theoretical considerations

That metallic mercury reduces mercuric mercury more or less completely to mercurous mercury can be proved by the formation of a white precipitate of mercurous chloride on the surface of clean mercury when the latter is introduced into a solution of mercuric chloride. In fact this is one of the laboratory methods of preparing calomel.

The ratio Hg(ous):Hg(ic) is controlled by the equilibrium of the reaction $Hg^{++} + Hg = Hg_2^{++}$. Mercury, being present in large quantities, is the stabilizing factor in this equilibrium but it can, by virtue of its globular size, change this ratio to an appreciable extent. We have already calculated the maximum ratio of Hg(ous):Hg(ic) as 216.7 from a thermodynamic standpoint entirely. This ratio corresponds to that created by a large body of liquid mercury and would be the same whether the equilibrium was approached from a solution of pure mercurous ion or mercuric ion.

Lewis and Randall (3) have deduced an equation,

$$F - F^0 = \frac{2\gamma V}{r}$$

showing the reciprocal relationship between the increase in free energy of a drop of liquid and its radius. In the equation F is the molal free energy of the drop, F^0 that of a large body of the liquid, γ is the surface tension of the large body of liquid, V is the molal volume, and r is the radius of the drop.

Qualitatively, thus, Hg would become increasingly more important in the equation $Hg^{++} + Hg = Hg_2^{++}$ as its state of subdivision increased, i.e., as its radius decreased, and we should expect a greater ratio of Hg(ous): Hg(ic) or a lower electrode potential as a result of this.

EXPERIMENTAL

By mechanical agitation one can obtain mercury in a sufficiently small state of subdivision to detect the change in E.M.F. resulting, but barely so. One has to resort to chemical means to obtain mercury globules of small enough radius to observe an appreciable effect.

To obtain mercurous sulfate absolutely free from mercury is a difficult task. The electrolytic and chemical preparations almost invariably contain some free mercury. The crystalline product should contain none but it is difficult to prepare by the usual recrystallization methods. A simple method (4) has recently been devised whereby gaseous sulfur dioxide is allowed to diffuse slowly into a sulfuric acid solution (1:6 acid) which is about 75 per cent saturated with respect to mercuric sulfate (about 350 grams per liter). If the sulfur dioxide diffusion is slow enough the Hg_2SO_4, which is formed by reduction and is comparatively insoluble in the acid, does not come out as a precipitate but grows into well-formed plates. This material must be well washed with 1:6 H_2SO_4 and the electrolyte to be used.

Cells, whether cadmium or zinc, built with this mercury-free crystalline mercurous sulfate have high E.M.F.'s (taking the E.M.F. of mercury-laden electrolytic mercurous sulfate as normal). There are two phenomena to consider, with respect to the crystalline and electrolytic preparations. First, there is the effect of the particle size on the solubilities of two materials. The crystalline material has an average size of 500 microns, while the electrolytic material has a particle size of 1 micron. On the basis of this we should expect the solubility (5) of the former to be less than that of the latter, and, in view of equation a above we should expect the E.M.F. of the former to be smaller than that of the latter. However, just the contrary is true of the E.M.F., and so it is necessary to explain the difference by virtue of the effect the interspersed mercury in the electrolytic material has on the Hg(ous):Hg(ic) ratio and the consequent change in E.M.F. as calculated from equation c. This second phenomenon masks the first one quite completely.

The behavior of a typical saturated cadmium and zinc cell built with mercury-free crystalline mercurous sulfate, follows:

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day	1 018432 volts	1 420234 volts
5 days	1 018327 volts	1 420200 volts
25 days	1 018289 volts	
46 days	1 018255 volts	1 420214 volts
64 days	1 018229 volts	

The cadmium saturated cell shows the decline in E.M.F. characteristic of those cells made with large crystalline mercurous sulfate (6).

The above data can be contrasted with the following data for two cells built with electrolytic Hg_2SO_4:

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day		1.419980 volts
7 days	1.018122 volts	1.420000 volts
14 days	1.018114 volts	1.420004 volts
21 days	1.018113 volts	1.420031 volts
28 days	1.018114 volts	1.420034 volts

During the course of our exploration of the E.M.F. at various points in the electrolyte of old cells, the E.M.F. in the Hg_2SO_4 paste itself was examined and almost invariably it was lower than the E.M.F. of the large mercury electrode below. The mercurous sulfate in these cells was electrolytic product and contained much free mercury of small globule size, but at the cell's mercury electrode surface only a very large area of mercury of a small degree of curvature was existent. In the paste, therefore, we should expect the mercuric ion to be more repressed than at the surface of the mercury electrode and the E.M.F. to be smaller in the first case, which is observed.

	E.M.F. of cell	*E.M.F. in paste*
Cell G9 (4 years old)	1.018280 volts	1.017930 volts
Cell G17 (2 years old)	1.018140 volts	1.014790 volts
Cell G3 (4 years old)	1.018120 volts	1.017910 volts

The effect of very finely divided mercury on a cell's E.M.F. was emphasized by preparing a very black mercurous sulfate by a prolonged passage of sulfur dioxide into an acid solution of mercuric sulfate and using this product in cells which gave very low E.M.F.'s.

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day	1.017366 volts	1.418589 volts
4 days	1.018036 volts	
11 days	1.018036 volts	
32 days	1.018103 volts	
47 days		1.419734 volts

All of the cells built with this material show marked recuperative powers toward the normal E.M.F.

A very light coating of finely divided mercury was deposited on a sample of clear crystalline mercurous sulfate by running two 5-cc. portions of 1:6 H_2SO_4, 40 per cent saturated with sulfur dioxide at atmospheric pressure and room temperature, through the sample while on the filter. The crystals turned gray on the surface. Acid saturated cells were made of this material. The electrolyte was about 0.08 molar in H_2SO_4 to prevent effects due to hydrolysis These cells likewise had low original values.

Time after construction	E.M.F.	*E.M.F. corrected to neutral solution*
1 day	1.016840 volts	1.016972 volts
3 days	1.017182 volts	1.017314 volts
2 days	1.017924 volts	1.018056 volts

The fact that cells built with finely divided mercury present in the depolarizer tend to increase in E.M.F. is quite concordant with theory. We have shown that the free energy of the spheroids of mercury and, therefore, their vapor pressure increases as the radius decreases. In obedience to the universal law that everything tends toward a state in which its free energy is a minimum, the smaller globules of mercury are continuously "distilling over" to larger ones of a smaller free energy. As this process continues the importance of the mercury in the equation $Hg^{++} + Hg = Hg_2^{++}$ becomes less, and the E.M.F. rises to the normal value. When the electrolytic method of preparing mercurous sulfate was developed (7), it was found that much finely divided mercury was formed at the mercury anode and attached itself to the mercurous sulfate, giving it a gray appearance. At that time it was our practice to stir the mercurous sulfate in the acid electrolyte together with excess mercury with the object of eliminating any finely divided particles of sulfate that might give an abnormal solubility. Now it seems that this procedure accomplished another important end. The very finest mercury globules also disappeared, as indicated above, and only those of a certain size remained, but these mercury globules appear to establish the equilibrium $Hg^{++} + Hg = Hg^{++}$ more rapidly and certainly than does the bulk mercury of the electrode, and this equilibrium determines the reproducibility of cells. Evidently much finely divided mercury should be present in the "paste," but it should be equilibriated by several hours (over night) stirring with sulfuric acid and excess mercury.

REFERENCES

(1) Hulett and Elliott: Diffusion in Standard Cells J. Phys Chem. **37**, 245 (1933).

(2) Summers and Gardiner: Trans. Am. Electrochem Soc. **56**, 141 67 (1929).

(3) Lewis and Randall: Thermodynamics, pp. 251-2. McGraw-Hill Book Company, New York (1923).

(4) Elliott and Hulett: J. Phys. Chem. **36**, 2083 (1932).

(5) Hulett: The Solubility of Gypsum. J. Am. Chem Soc **24**, 667 (1902).

(6) Gardiner and Hulett: Trans. Am. Electrochem. Soc **56**, 111 28 (1929). The Hydrolysis of Mercurous Sulfate.

(7) Carhart and Hulett: Trans. Am Electrochem. Soc **5**, 59 (1904).

ON THE FORMATION, SIZE, AND STABILITY OF EMULSION PARTICLES. I

A NEW METHOD OF EMULSIFICATION

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I. GENERAL METHODS OF EMULSIFICATION

In general, the formation of a disperse system may be achieved in two distinct ways: (a) by mechanical disintegration of bulk material into the fine particles forming the disperse phase, (b) by condensation of molecules of the disperse phase into larger aggregates, either process taking place in the presence of the dispersion medium. This fact is fully recognized in general colloid chemistry, where both types of method are in use, although condensation methods are there of chief importance. On the other hand, in the study of emulsions little attention has been paid to the possibility of utilizing condensation methods of preparation, mechanical dispersion being almost invariably employed. We shall here consider chiefly emulsions containing an emulsifying or stabilizing agent; since in such systems the added substance produces an interfacial phase between the two liquids, these emulsions will be described as "three-phase" emulsions, in contrast with "two-phase" systems where only the pure liquids are present.

Two modifications of the dispersion method are possible in emulsification: (a) the whole of the two liquids forming the emulsion may be agitated together for a suitable time in the presence of an appropriate emulsifying agent, either in one operation or with gradual addition of the liquid which is to form the disperse phase; (b) the latter liquid may be injected into the medium containing a stabilizing agent as a stream of fine droplets. The former means is almost invariably used, although it is theoretically inefficient and open to grave objections; it has been criticized by Clayton (1).

The processes taking place in the agitation method have been considered by Stamm and Kraemer (2). The formation of the emulsion is the net result of two opposing forces: the effect of agitation in disrupting the liquids, and the tendency to re-coalescence with the formation of bulk phases. Both liquids are broken up, and the degree of subdivision of each will be conditioned by mechanical factors such as the mode of agitation, the volume ratio, densities, and viscosities of the liquids, and the interfacial tension. Formation of an emulsion depends on the re-coalescence of only one liquid to a continuous phase, the second liquid remaining subdivided after agitation ceases. The chief function of the emulsifying agent is to inhibit coalescence of the internal phase during and after emulsification, although in so far as its presence affects the mechanical properties of the liquids, it will affect the dispersion process. In particular, the reduction in interfacial tension which is produced by substances capable of acting as emulsifying agents will assist disintegration of the phases. Either an oil-in-water or a water-in-oil emulsion may be obtained as a stable system, by suitable choice of the emulsifying agent.

For the description and critical discussion of the various methods of agitation or stirring used for emulsification, reference should be made to Clayton's publications (1). It may be mentioned that according to recent experiments (3, 4), agitation by mechanical means may be replaced by irradiation by ultrasonic waves of the order 200 to 500 kilocycles per second, many different emulsions having been prepared in this way.

Since in the final emulsion only one liquid is subdivided, energy expended in breaking up the medium is entirely wasted, and greater efficiency is to be obtained in emulsification by injection of the internal phase, already broken up into droplets, into the bulk of the medium containing the stabilizing agent (3a). "The whole work of dispersion can thus be made on the internal phase and adsorption at the dineric interface can be reached without the interfering adsorption at the gas-liquid boundary common to the usual agitation or stirring methods" (Clayton 1b). In this method the degree of dispersity or particle size will be fixed by the method of breaking up the internal phase, and the function of the stabilizing agent will lie mainly in preserving the individuality of the particles introduced into the medium.

Three possible methods may be considered for the formation of emulsion particles by condensation from a state of molecular subdivision, according as the molecules are derived from (1) a vapor phase, (2) true solution, (3) chemical action. The two latter methods, when applicable, introduce complications, owing to the presence of unwanted solvents or reaction products. Lewis (4) obtained a dilute emulsion of mineral oil in water by pouring an alcoholic solution of the oil into water. No stabilizing agent was used, the product being a two-phase emulsion or oil hydrosol, but the same method could be employed for obtaining a more concentrated three-phase emulsion. Chemical methods are of considerable importance in general colloid chemistry, being often the only means of obtaining certain sols, but this is not the case with emulsions. A case of interest is the formation of an oleic acid-in-water emulsion by the addition of mineral acid to a solution of sodium oleate. If the acid is not in excess, the residual soap acts as a stabilizing agent.

Methods involving condensation from a vapor phase fall into two types, according as (a) the vapors of both disperse and continuous phases are brought into admixture and condensed, or (b) the vapor of the disperse phase is injected below the surface of the bulk of the medium. These correspond roughly with the two types of dispersion method. Both have been applied to the production of sols and two-phase emulsions. Roginsky and Shalnikoff (5) obtained sols of the alkali metals in organic liquids by condensing the vapors of liquid and metal on a surface cooled with liquid air, subsequently allowing liquefaction to take place. Lewis (4) obtained dilute two-phase emulsions (oil hydrosols) by boiling oil and water together under a reflux condenser, and by steam distilling aniline. As with the agitation method of emulsification, formation of a disperse system depends on the coalescence of only one component to a continuous phase. Method b has been employed by Nordlund (6) for the production of mercury hydrosols, and by Gutbier (7) for sols of sulfur, selenium, and mercury. The so-called "electrical dispersion" method of preparing metallic sols is essentially similar. the production of metallic vapor by an electric arc below the surface of the medium replacing injection from an external source.

Hitherto, the preparation of three-phase emulsions by condensation of vapor of the internal phase in the presence of a stabilizing agent has not been investigated. For this purpose method b is required, and in the next section the study of such a method of emulsification will be described. The results show that it is of considerable theoretical interest, and where it can be applied, it is of practical value in obtaining emulsions of very uniform grain.

II. A VAPOR CONDENSATION METHOD OF EMULSIFICATION

Emulsification being the preparation of a disperse system, the particle size or degree of dispersity is the criterion by which must be measured the efficiency of the process and the influence of various factors on it. In these experiments emulsification was effected by forcing oil vapor through a single capillary jet dipping below the surface of the aqueous phase contained in a beaker. The emulsion system was benzene in water, the stabilizing agent being sodium oleate. The size distribution of particles in each emulsion was determined by an improved sedimentation method based on those of Kraemer and Stamm (8) and of Lambert and Wightman (9), a sedimentation tube being used in conjunction with an automatic photographic recorder. The technique of this method has been fully described in a separate paper by the present author (10).

The dispersity of an emulsion made by passing a stream of oil vapor into an aqueous liquid may be influenced by factors of two kinds: (1) the conditions of injection, (2) the physico-chemical properties of the emulsion components. Factors of the first kind include the temperature and pressure of the vapor on entry, and the dimensions of the orifice through which it issues. The pressure of the vapor and the dimensions of the jet control the velocity of the vapor, and in this connection two quantities must be considered, viz., the linear velocity imparted to the molecules, and the mass or volume of vapor passing per second. The effects of all these conditions have been studied. In addition, the temperature and volume of the medium and the shape of the container may be relevant. Factors of the second kind include the chemical nature and physical properties of the liquids and stabilizing agent, the volume ratio of the liquids in the final emulsion, the concentration of stabilizing agent, etc. As indicated, the experiments cited have been confined to a single system, and of the conditions named, the concentration of sodium oleate has received chief attention.

Apparatus

In order to control the conditions of injection of the vapor, the apparatus shown in figure 1 has been developed. Benzene is boiled by means of the heating coil A in the vessel B, which is provided with a trap bulb C. The vapor passes through the delivery tube D, jacketing the cylindrical bulb E which is filled with nitrogen, to the bulb F. For clearness of drawing, the apparatus has been dissected in figure 1; in actual front view D is immediately behind F, the connecting tube (shown dotted) being about 8 cm. long so as to leave a clear space below the jet. The vapor finally emerges via the trap G through the jet H. From C nearly to H, the tube is wound with nichrome wire on asbestos paper. All parts of the apparatus which are subjected to heat are lagged by winding with asbestos string. The temperature of the vapor is read on the thermometer J cemented into the bulb F, and the pressure on the manometer K, both values being measured as near as possible to the jet.

The bulb E forms a nitrogen thermoregulator, and operates a mercury contact L controlling the relay M, which in turn controls the current through the superheater coil. The temperature at which the regulator works is determined by adjustment of the nitrogen pressure by means of the mercury column N, the whole arrangement being essentially a constant volume gas thermometer. In this way the temperature of the issuing vapor may be maintained at any arbitrary constant value. Automatic regulation of the pressure is provided by adjusting the contact P of the manometer to the desired value. This controls the current through the heating coil A by means of the relay Q. Since the rate of vapor formation governs the rate of efflux, equilibrium being reached at a pressure such that these two rates are equal, maintenance of a constant pressure is dependent on a steady rate of boiling, and this is achieved by the arrangement described. Power is taken from the mains (200 volts, D.C.), and a relay circuit already described by the author (11) is used; except that whereas the relay Q brings extra resistance into the heating circuit when contact P is closed, as in the published arrangement, relay M does so when contact L is opened.

Taps are included in the apparatus at suitable points, for filling and draining the boiling vessel, for setting up and also for isolating the two manometric systems, and for draining distilled benzene from the bulb S. No tap is exposed directly to vapor.

A special device is used for introducing the beaker of dispersion medium quickly and accurately beneath the efflux jet. This comprises a stage T which is moved vertically by means of a rack and pinion U, and may be held in any desired position by a quick-release pawl (not shown). The beaker is placed on the stand, and the latter is quickly raised until the jet just dips into the liquid. After the required amount of vapor has been passed, the pawl is released, the stand quickly lowered, and the beaker withdrawn.

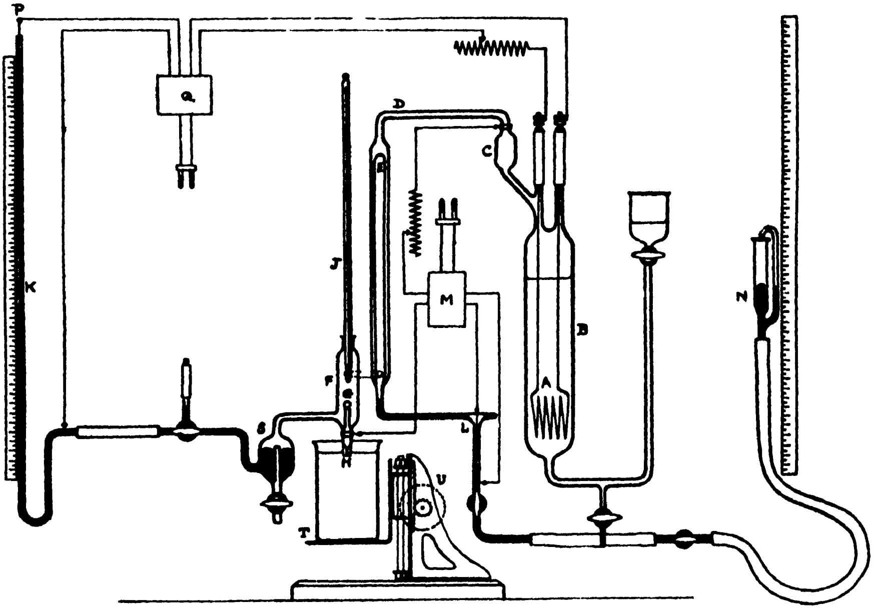

FIG. 1. EMULSIFICATION APPARATUS

The procedure in an experiment was as follows. The emulsification apparatus was started up and the oil vapor allowed to issue into pure water until a steady state was reached, under the desired conditions of temperature and pressure. A known volume of the dispersion medium, at a known temperature, was then quickly substituted for the water, and vapor was allowed to pass for the required time. The temperature of the emulsion having been noted, the beaker was then transferred to a special device in a water thermostat at 25°C., where the emulsion was kept stirred without free access of air. When temperature equilibrium was reached, a quantity of the emulsion was rapidly transferred to the sedimentation tube, previously set up in an air thermostat at 25°C. Another portion of the fresh emulsion was utilized for a pycnometric determination of its density (also at 25°C.), whence its composition was calculated from the known densities of oil and medium.

Materials

The benzene used was Kahlbaum's "crystallized thiophene-free" quality, without further treatment. It was recovered after use by allowing the emulsions to settle out, shaking the separated "cream" with water and benzene in bulk. The water phase was run off and replaced by pure water after each separation, and by repeating the treatment the concentration of soap was progressively reduced until the cream was entirely broken. The separated benzene was dried over sodium sulfate and redistilled, after which it was used in further experiments.

Sodium oleate was made from Kahlbaum's oleic acid, further purified by formation of the lead salt and extraction with ether, followed by hydrolysis and distillation of the acid *in vacuo*. The first sample of the sodium salt was prepared by neutralization of the acid in alcoholic solution with a slight excess of solid anhydrous sodium carbonate; the soap was extracted by repeated hot filtration, crystallization, and resolution in absolute alcohol. Superior results were obtained by the method of Harkins and Beeman (12); sodium ethylate made by dissolving sodium in alcohol was added to the acid (also in alcohol) until neutrality to phenolphthalein was reached. The salt was recrystallized from alcohol and finally dried for two days at 25°C. A 0.01 molar solution was made up in the cold and diluted as required; only a small quantity (100–250 cc.) was prepared at a time, in order to avoid waste due to deterioration on standing. Conductivity water was used throughout.

Conditions of emulsification

The capillary jet employed throughout had a diameter of 0.7 mm., giving a cross-section of 0.0038 sq. cm., and the length of the cylindrical portion was about 9 mm. With these dimensions, the times required under various pressures for the injection of 15 cc. of benzene into 135 cc. of solution, to form 150 cc. of a 10 per cent emulsion, were found to be as follows.

Pressure (mm. of mercury)	25	50	100	150
Time (minutes)	8½	5	3	2½

The velocity was thus not a linear function of the pressure, and since any substantial increase in velocity would evidently require a considerable increase of pressure, experiments were limited to the range given.

In one series of experiments, the orifice was reduced in diameter by cementing over the end of the capillary a disc of thin zinc foil, pierced with a fine hole. A solution of celluloid in amyl acetate was used for this purpose, so that the disc was readily removable. The diameter of the orifice was then 0.48 mm., the cross-section being 0.0018 sq. cm. The corresponding pressure-time relation was as follows.

Pressure (mm. of mercury)	50	100
Time (minutes)	11	6½

For a given pressure, the times with the two orifices were very nearly in the ratio of the respective areas, so that the linear velocity of the vapor was practically unaltered by reducing the opening. This fact enabled the effects of orifice diameter and linear velocity to be separated.

The temperature of the vapor remained constant to within ±1.5°C. during each experiment; in separate experiments the mean temperature corresponding with a given nitrogen pressure was not exactly reproducible, varying over a range of about 5°C. In order to control this as far as possible; the technique was standardized. First the superheater was switched on, and left for 30 minutes before heating of the benzene was begun. A further 15 minutes was allowed for equilibrium to be reached before the vapor was allowed to pass into the experimental solution.

Determination of size distribution

The results of the sedimentation analysis were plotted with time as abscissa and the reading of the index as ordinate. The size distribution was derived by drawing tangents to the curve, as described in the paper cited (10). In most of the following data, radius intervals of 1μ have been taken; the intercepts cut off the vertical axis by tangents drawn at the calculated points were read from the curve, and the results tabulated as the fractions of the total mass of disperse phase lying between given size limits. This fraction was obtained as the ratio between the intercept corresponding with the given interval, and the length cut off the axis by the limiting tangent, i.e., the tangent to the curve where the movement of the index became the steady drift due to evaporation. (It had been found that a linear relation held between the movement of the index and the mass of particles sedimented.) Any error involved in assuming that sedimentation was complete when the movement of the index became uniform would be slight, since observation of the sedimented emulsion after the experiment showed that the mass of any fine particles not included in the cream must be extremely small. A certain number of failures in sedimentation analysis were registered, through stoppage of the automatic mechanism, temperature irregularities due to faulty working of the thermostat, or bubbles in the index tube.

Reproducibility

The first experiments were carried out under the following conditions: vapor temperature 95–100°C., pressure 50 mm. of mercury, concentration of sodium oleate 0.0005 *M*, volume of solution 135 cc., time of passage of vapor 5 minutes. These constants proved to be convenient and were used to test the reproducibility of the emulsions, and also at various times as a check on the experiments. In consequence, this group of experiments forms the largest series corresponding with one set of conditions. The results are collected in table 1.

TABLE 1

EXPERIMENT	ΔS				
	$< 4\mu$	4–5μ	5–6μ	6–7μ	$> 7\mu$
1	8	21	32	21	18
2	–	38	32	13	17
3	8	34	29	16	13
4	4	31	32	15	18
13	11	36	32	12	9
15	10	28	35	12	15
17	5	40	29	13	13
Mean......	6	32	32	15	15

In table 1 ΔS represents the percentage of the total mass of particles corresponding with the radius intervals shown. Considering the nature of the process under investigation, the concordance of these results is excellent. The distribution varies slightly, but in all cases about 80 per cent of the mass of particles corresponds with the range 4μ to 7μ (the limits being 75 to 83 per cent). For an emulsion this is an extremely uniform dispersion, but it will be seen that even greater homogeneity has been obtained by the use of a higher vapor velocity.

Influence of conditions of injection

(*a*) *Vapor pressure.* The results obtained under various pressures, using the same orifice, vapor temperature, solution concentration, and oil concentration (10 per cent by volume) as before, are shown in table 2.

Table 2 would appear to show a progressive decrease in the mean particle radius with increase of pressure, but examination shows that this is due to a closing up of the limits of size, radii less than 4μ in no case passing the lower limit 3.5μ. The effect of an increase of pressure was therefore to produce a more uniform dispersion. It is remarkable that with pressures of 100 mm. and over, about 80 per cent of the mass of particles lay within the range 4μ to 6μ; moreover, at 100 mm. substantially the whole range of sizes was from 3.5μ to 6.8μ (approximately), and at 150 mm. from 3.5μ to 6μ.

TABLE 2

EXPERIMENT	PRESSURE	ΔS				
		< 4μ	4-5μ	5-6μ	6-7μ	> 7μ
	mm					
11	25	—	11	18	18	53
14	25	3	10	30	21	36
Mean		1½	10½	24	19½	44½
Mean*	50	6	32	32	15	15
6	100	16	52	27	5	—
7	100	11	54	26	9	—
Mean		13½	53	26½	7	—
9	150	19	55	26	—	-
10	150	17	50	33	—	—
Mean		18	52½	29½	—	—

* From table 1.

TABLE 3

EXPERIMENT	PRESSURE	TEMPERATURE	ΔS				
			< 4μ	4-5μ	5-6μ	6-7μ	> 7μ
	mm	*degrees C*					
15	50	100	10	28	35	12	15
16	50	115	10	33	34	12	11
18	50	135	7	38	27	19	9
19	50	156	8	22	34	27	9
Mean			9	30	32	18	11
Mean*	100	96	13½	53	26½	7	—
22	100	117½	17	45	33	5	—
20	100	134	14	46	33	7	—
21	100	156	14	49	32	5	—
Mean			15	48	31	6	—

* From table 2.

(*b*) *Vapor temperature.* Experiments were carried out over the range of temperature 96°C. to 156°C. (16°C. to 76°C. above the boiling point of benzene), using steps of from 15 to 20 degrees, for each of the pressures 50 mm. and 100 mm. The results are given in table 3.

It is evident from the figures in table 3 that the temperature of the vapor was without effect on the distribution of particle sizes.

(*c*) *Orifice diameter.* In these experiments the capillary jet was as before, except that the orifice was reduced by cementing over the end a perforated disc of zinc foil. The results are shown in table 4.

By comparison of table 4 with table 2, it is seen that the efficiency of emulsification with the higher pressure was not considerably altered by a reduction in the cross-section of the orifice, the size range of the particles remaining about the same. A somewhat higher percentage of the total mass corresponded with the interval 4μ to 6μ, but of this a larger proportion lay in the interval 5μ to 6μ, while there was a decrease in the fraction between 3.5μ and 4μ, and an increase in that between 6μ and 7μ. With the lower pressure, there was a reduction in the fraction lying between 4μ and 7μ, owing to an increased proportion of large particles.

TABLE 4

EXPERIMENT	PRESSURE	AS				
		< 4μ	4–5μ	5–6μ	6–7μ	> 7μ
	mm					
23	100	7	48	35	10	–
24	100	–	45	43	12	–
Mean		3½	46½	39	11	–
25	50	–	23	30	17	30
26	50	3	27	29	16	25
Mean		1½	25	29½	16½	27½

The effect of orifice diameter, therefore, became less noticeable as the pressure was increased.

Since it was found that the linear efflux velocity of the vapor was not greatly affected by a reduction in the size of the orifice, it would appear that the linear velocity was of more importance than the mass or volume velocity. This suggests that the uniformity of dispersion was largely dependent on an efficient distribution of vapor throughout the condensation zone rather than on the actual amount injected per second. With a view to obtaining some idea of the conditions of mixing, the linear and volume velocities under the experimental conditions have been calculated from the observed mass velocity and orifice diameter (see table 5). Since the gss laws have been used for this purpose in default of empirical information as to the specific volume of benzene vapor at various temperatures and pressures, the figures are necessarily very approximate, and useful only for comparison purposes.'

The figures in table 5 show clearly the predominant importance of the linear velocity. Thus the larger jet in conjunction with a pressure of 50 mm. gave roughly the same momentum as the smaller jet and a pressure of 100 mm., while the actual mass of volume of vapor emerging per second was greater in the former case; notwithstanding this, the higher pressure gave more efficient dispersion. The uniformity of the dispersion clearly increased as the linear velocity of the vapor rose, but had no obvious connection with any of the other factors.

(*d*) *Other conditions.* The volume of solution and the shape of the container might be expected to influence the condensation process through their effect on the conditions of mixing, if condensation of the vapor occurred throughout the liquid. Actually, it was observed that condensation occurred in the neighborhood of the jet, the drops formed then distributing themselves throughout the whole volume of liquid. Thus as far as the actual condensation was concerned, the liquid was effectively without limit, so that the actual boundaries were unimportant.

TABLE 5

ORIFICE	PRESSURE	m*	V	u	mu
	mm				
I	25	0 025	9 2	2400	59
	50	0 044	16	4200	190
	100	0 074	26	6700	500
	150	0 085	28	7200	600
II	50	0 020	7 1	3900	778
	100	0 033	11	6400	210

* Here m = mass of vapor passing per second, in grams (observed), V = volume of vapor per second, in cubic centimeters (calculated), u = linear velocity at orifice, in centimeters per second (calculated), $mu = m \times u$ = momentum at orifice, in gram centimeters per second (calculated).

The influence of the initial or mean temperature of the solution has not been studied experimentally, but may be inferred. The effect of raising the temperature may be expected to depend chiefly on the consequent reduction in viscosity and in interfacial tension. The former will facilitate the passage of vapor or of drops through the liquid, and so will have the effect of a higher linear velocity, while the latter will probably have a similar effect to that of an increased concentration of soap. It may be mentioned that in the experiments described, the temperature of the solution during emulsification rose by about 10–12°C.

Influence of soap concentration

(*a*) *Initial concentration.* In these experiments the concentration of soap in the solution was varied over the range 0.0005 *M* to 0.0025 *M*. For each of the concentrations 0.0010, 0.0015, 0.0020, 0.0025 *M*, two experiments were performed; one of the records for 0.0015 *M* showed a disturbance of the sedimentation, but as it gave good qualitative agreement with the satisfactory record, the experiment was not repeated. The figures for 0.0005 *M* are from previous experiments. In all cases the unobstructed jet was used, the pressure being 100 mm. and the vapor temperature 95–100°C. As in previous experiments the concentration of benzene in the emulsion was as nearly as possible 10 per cent. The results are shown in table 6, a more detailed analysis of the size distribution being given in order to bring out clearly the effect of the concentration of solution used in the emulsification process.

TABLE 6

EXPERIMENT	CONCENTRATION	ΔS								
		2-2.5	2.5-3	3-3.5	3.5-4	4-4.5	4.5-5	5-5.5	5.5-6	> 6μ
	M									
6	0.0005	—	—	—	16	21	31	17	10	5
7	0.0005	—	—	—	11	24	30	18	8	9
Mean		—	—	—	13½	22½	30½	17½	9	7
28	0.0010	—	—	5	24	32	26	10	3	—
29	0.0010	—	—	4	19	35	20	14	8	—
Mean		—	—	4½	21½	33½	23	12	5½	—
32	0.0015	—	5	22	20	30	14	9	—	—
30	0.0020	—	20	24	29	17	10	—	—	—
31	0.0020	—	16	25	30	18	11	—	—	—
Mean		—	18	24½	29½	17½	10½	—	—	—
27	0.0025	5	34	36	11	9	5	—	—	—
33	0.0025	6	23	41	15	15	—	—	—	—
Mean		5½	28½	38½	13	12	2½	—	—	—

It is evident from table 6 that with increasing concentration there was a continuous downward trend of the mean particle radius. This effect is quite distinct from that due to increasing pressure, for in this case the range of sizes was not reduced appreciably, but was shifted as a whole. The phenomenon was shown very clearly by even a qualitative inspection of the sedimentation records, since the time of sedimentation varies inversely as the square of the particle radius.

Over the range of concentration investigated, the optimum interval was reduced from 4.5–5μ to 3–3.5μ. There is no indication in these results as to the limiting size obtainable by further increase in concentration; extension in this direction became difficult owing to the greatly increased time required for sedimentation, in accordance with the relation (Stokes' law) mentioned above. For 0.0005 M solutions, a complete sedimentation record covered a period of twenty to twenty-four hours; for 0.0025 M, about fifty hours. The fact that dispersions having distinct size limits within such a small range could be reproduced at will is an indication of the accurate definition of conditions which is possible in this method of emulsification.

(*b*) *Effect of additions of soap after emulsification.* It was noticed that on standing for a day or so, an emulsion formed as above showed a coarsening of the dispersion. With 0.0005 M soap solution, the cream in the sedimentation tube had almost invariably broken to some extent by the end of the experiment. Over the same period the emulsion filling the pycnometer tube showed no breaking, but on redistributing the cream throughout the liquid, the uniform emulsion was less opaque than originally. Similar coarsening without breaking was found when a stoppered cylinder completely filled with the emulsion was left to stand, so that the behavior in the sedimentation tube must be ascribed to the presence of an air phase above the liquid, other conditions being the same. This is in agreement with the fact noted by Clayton (1b), that emulsions can be broken by shaking if a gaseous phase is present.

In explanation of the observed decrease in dispersity, it was supposed that the amount of soap present, while able to promote emulsification, must be insufficient to prevent coalescence of the oil droplets over a prolonged period, especially when the emulsion was allowed to cream so that the droplets came into close contact. This suggested that enhanced stability might be achieved by further addition of soap, and a series of experiments was carried out, in which was examined the effect of increasing the soap concentration *after* emulsification.

A known volume, V, of 0.0005 M sodium oleate solution was used to prepare an approximately 20 per cent emulsion, under fixed conditions of temperature and pressure, and to this emulsion was added an equal volume, V, of x molar sodium oleate solution, x being variable. A 100-cc. stoppered cylinder was completely filled with the resulting emulsion of 10 per cent benzene in $\frac{1}{2}$ $(x + 0.0005)$ M solution, and left to stand in a thermostat at 25°C. for from forty-four to forty-eight hours. The emulsion was then mixed uniformly again and a sedimentation analysis carried out. For comparison purposes were taken 10 per cent emulsions in 0.0005 M solution, made not directly but by dilution of a 20 per cent emulsion with the same medium. One such emulsion was sedimented immediately, and a similar one after two days. This gave directly the effect of ageing on the original emulsion, while additions of 0.0015, 0.0025, 0.0035, 0.0075 M solution showed the behavior in contact with concentrations of 0.0010, 0.0015, 0.0020, and 0.0040 M, respectively.

The results may be shown best, not by analysis of the sedimentation curves but by plotting these directly on the same graph, as in figure 2. This shows time as abscissa, and the percentage of the total mass of particles which have settled out, as ordinate. It will be seen that the original emulsion showed a great increase in the velocity of sedimentation (and hence in particle size) as the result of standing, but that with increasing soap concentration the sedimentation velocity of an aged emulsion decreased and the curve approached that of a fresh emulsion. Over the range examined, however, this curve was not reproduced for an aged emulsion.

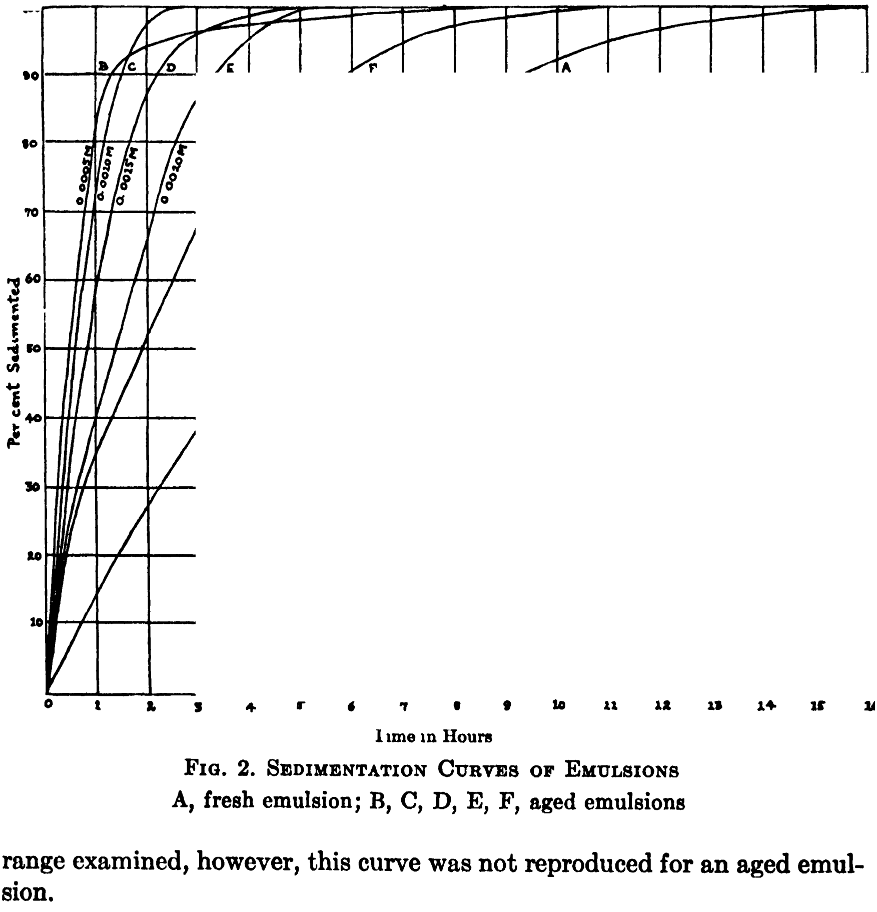

FIG. 2. SEDIMENTATION CURVES OF EMULSIONS
A, fresh emulsion; B, C, D, E, F, aged emulsions

Consideration of the effect of soap concentration on the stability of emulsion particles is reserved for a later paper. For the present purpose it is sufficient to notice that in this condensation method of emulsification, it is of prime importance whether the final soap concentration is fixed before or after the emulsion is made. The dispersity of the emulsion is governed by the initial concentration. It is evident that the size and number of the particles formed in the emulsification have no direct relation with the area of interface which may be maintained over a prolonged period of time, for on raising the initial soap concentration the dispersity (and hence the interfacial area) increases, in spite of the fact that at the lower concentration this area is too great for stability. Thus in passing from 0.0005 *M* to 0.0025 *M* solution, the interfacial area was augmented by about 50 per cent; nevertheless a concentration of 0.0040 *M* was insufficient to keep the lower area stable for two days. It must be concluded that the soap exercises two distinct functions: (1) in the formation of the emulsion; (2) in the stabilization of the emulsion. The second function does not depend on the method of preparation, and will be the same for an emulsion of given properties (dispersity, volume ratio, soap concentration), however it is made. On the other hand, the first function is characteristic of the method of emulsification. In the present method the soap concentration has a direct influence on the dispersity of the emulsion, and a physcochemical equilibrium in the condensation process must be postulated. The question then arises: what is the function of the emulsifying agent in other methods of emulsification? This function, and the influence of the emulsifying agent on emulsion stability, will be considered in a later paper.

III. THEORY OF THE CONDENSATION PROCESS

Possible mechanisms

In an attempt to ascribe a mechanism to the formation of emulsion particles by this method, two possibilities must be examined· (1) bubbles of vapor may be produced by the breaking up of a cylinder of vapor formed by the jet, these bubbles then condensing to liquid droplets; (2) particles may be produced by the growth of nuclei spontaneously formed in a supersaturated system of oil molecules. The latter case may be further subdivided, according as condensation takes place in the vapor or in the liquid phase, i.e., oil vapor may condense within water vapor, the droplets being then taken up by the medium, or oil molecules may aggregate to particles in direct contact with the aqueous liquid.

The observed results do not support the first hypothesis. The stability of a cylinder of fluid was investigated by Plateau (13), who showed that when the length exceeded the circumference, instability set in, a long cylinder breaking into drops, the distance between whose centers was equal to the circumference of the cylinder. A small globule was formed between each pair of large drops. Neglecting the volume of the small drop, the radius of the large drop is seen to be $a\left(\frac{3}{2}\pi\right)^{1/3}$, *a* being the radius of the cylinder. The drop radius should be directly dependent, therefore, on the jet radius, which was found not to be the case. Moreover, it may be calculated that of the orifices used, the larger should give liquid droplets having radii of the order 80μ, and the smaller one radii of the order 60μ, both of which values are considerably larger than the observed size. Still more does this latter fact exclude the alternative explanation that the break-up of the cylinder might form primary particles which would grow under conditions dependent on the properties of the medium, and we are led to the conclusion that the mechanism is of the second type.

The observed effect of soap concentration on particle size may be reasonably assumed to be due to the decrease in interfacial energy produced by the soap. If condensation to the final droplets occurred in the vapor phase, however, the only interface coming into account would be that between liquid oil and the mixed vapor of oil and water, whose surface tension would be independent of the soap concentration. There remains the possibility that primary particles might be formed in the vapor phase and might be taken up by the solution, there growing by coalescence with one another. This would mean that nucleus formation would be independent of the soap concentration but growth would not, since the ease of coalescence would depend on the interfacial tension. The variation in dispersity (which means the production of varying numbers of particles from a given mass of oil) must then depend on the degree of aggregation of primary particles.

On the other hand, the hypothesis that the whole process of condensation takes place in direct contact with the aqueous phase presents more analogy with the processes known to take place in other supersaturated systems, since the mechanism would then consist in the formation of primary particles or nuclei, which grow by accretion of other oil molecules independently of collision between the particles themselves. A variation in dispersity may then be caused by an alteration in the process of nucleus formation or in the rate of growth. Since the interface concerned is that between oil and aqueous solution, it is readily understandable that both the formation and growth of nuclei may be conditioned by the composition of the solution. This view of the process has been adopted provisionally, and will now be considered in some detail.

Nucleus formation

The experiments described differ from the ordinary case of condensation or crystallization in a supersaturated system, where the process starts from a certain initial supersaturation and goes to completion without the introduction of further material, for here there is a continuous addition of molecules to the system. It has been mentioned that the actual condensation takes place in a limited zone near the jet, so that the particles leaving the zone probably take no further part in the process. A steady state will therefore be set up, in which as much material leaves the zone in the form of particles as enters in the same time in the form of individual molecules. This will correspond with a certain degree of supersaturation in the condensation zone. Considering a single particle, the process may be regarded as comprising two stages, viz., the appearance of a nucleus, and its growth as it passes through the zone. The average size which a particle attains will depend on the velocity of growth and the time spent in the zone.

The formation of a nucleus means the collision and union of a number of molecules to an aggregate having the properties of surface, and this involves the generation of surface energy, which must be provided by the energy of condensation. Two conditions are therefore necessary: (1) a number, n, of molecules must be mutually so situated that they may condense together; (2) the condensation of these molecules to a particle must involve a net decrease in free energy. We will take the latter condition first. The formation of nuclei in any supersaturated system (vapor, solution, undercooled melt) will depend on similar factors, but for purposes of calculation the case of condensation in the vapor phase is the simplest to take, and will now be considered. In what follows the vapor is assumed to behave ideally.

It is shown readily that there is a minimum radius, which must be reached before a drop of liquid can grow by condensation of molecules upon its surface. W. Thomson (14) showed that the vapor pressure over a curved liquid surface increases with the curvature, the relation between p_x, the pressure over a spherical drop of liquid of radius x, and p_∞, the pressure over a plane surface of the same liquid, being

$$RT \ln \frac{p_x}{p_\infty} = \frac{2\sigma M}{d} \tag{1}$$

where M is the molecular weight, σ the surface tension, and d the density of the liquid. Following Gibbs, Volmer and Weber (15) point out that in consequence of this relation, in a vapor having a supersaturation pressure p_r, a drop having a certain radius r will be in equilibrium. Drops of smaller radius have a higher vapor pressure and are consequently unstable, while for radii greater than r the vapor pressure will be less than p_r and condensation on the drop will occur. A drop having the "characteristic radius" r corresponding with the supersaturation pressure p_r is defined by Volmer and Weber as a "nucleus," since under the given conditions it represents the lower limit of size for a drop capable of spontaneous growth. The work necessary to form such a drop within the vapor is shown to be

$$W = \frac{4}{3}\pi r^2 \sigma \tag{2}$$

or by substitution from equation 1

$$W = \frac{16\pi\sigma^3 M^2}{3R^2T^2d^2\left(\ln \frac{p_r}{p_\infty}\right)^2} \tag{3}$$

This work is taken as a measure of the stability of the supersaturated vapor.

Adopting this definition of a "nucleus," Farkas (16) has calculated the number of nuclei which overstep the characteristic radius r per second and grow to larger sizes. In the present writer's view, the production of drops having the "characteristic radius" is of secondary importance where the condensate is highly disperse, since the molecules forming such a drop must have energy above the average. The formation of a large number of nuclei[1] is only possible if molecules of average energy can condense together, and this may be achieved if groups containing a sufficient number of molecules are available. The idea of the "characteristic radius" may, however, be utilized in deriving the condition under which condensation of "average" molecules will occur.

Consider first the condensation of vapor on a plane surface of its own liquid, of constant area; let the vapor pressure of the liquid be p_∞ and the actual pressure of the vapor p_r. Since no surface work is involved in the change of state, the increase in free energy per molecule will be

$$w_\infty = kT \ln \frac{p_\infty}{p_r} \tag{4}$$

where k is Boltzmann's constant. Condensation will occur if w_∞ is negative, i.e., if $p_r > p_\infty$, while evaporation will occur if $p_r < p_\infty$. The condition $w_\infty = 0$ is realized when $p_r = p_\infty$, and corresponds with equilibrium.

When the liquid surface is curved, surface work is involved in the change of state, and this must be taken into account in the calculation. Consider the formation of a drop of liquid containing n molecules and having a radius x. The net increase in free energy is given by

$$\begin{aligned} W &= nw_\infty + 4\pi x^2\sigma \\ &= nkT \ln \frac{p_\infty}{p_r} + 4\pi x^2\sigma \end{aligned} \tag{5}$$

Now

$$nkT \ln \frac{p_\infty}{p_r} = -\frac{2\sigma}{r} \cdot \frac{M}{d} \cdot \frac{n}{N} = -\frac{2\sigma}{r} \cdot \frac{4}{3}\pi x^3 \tag{6}$$

where N is Avogadro's number, so that

$$W = 4\pi x^2\sigma \left(1 - \frac{2}{3}\frac{x}{r}\right) \tag{7}$$

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[1] This term is used to denote a primary particle of any size, and not in the above limited sense.

This equation reduces to equation 2 when $x = r$. W is negative when $x > \frac{3}{2} r$, and this is the condition for the formation of a nucleus by molecules of average energy.[2]

It is to be noted that when n is small, the drop cannot be regarded as spherical, and in order to apply these equations the idea of an "equivalent radius" must be introduced, i.e., x and r are then not actual dimensions of the drops but the radii which the respective drops would have if they were spherical. An uncertainty remains, in that the value of σ for such small drops is not necessarily the same as for larger drops.

A similar calculation may be applied to the case of a supersaturated solution. It has been found (17) that the solubility of small crystals is greater than that of large ones, in analogy with the vapor pressure of liquid drops, and an equation similar to equation 1 may be used, solubility or solution pressure being substituted for vapor pressure. In fact, in any change of state where surface energy is generated, there will be a critical radius below which particles cannot be formed by molecules of average energy.

The probability, P_n, that a group of n molecules will be formed, at a given temperature, is a function of the concentration (of uncondensed molecules) and of the number n, such that (a) for a given value of n, P_n will increase with the concentration, (b) with a given concentration, P_n will diminish as n is increased, both rates of change being greater than proportionality. To each concentration, therefore, two numbers may be assigned, where (1) n_1 is the least number of molecules in an aggregate, the probability for whose formation is less than a given very small quantity (and therefore representing the upper limit of size for a group), and (2) n_2 is the number of molecules in an aggregate for which the net change in free energy in condensation is zero, for molecules of average energy. If $n_1 < n_2$, nuclei will not be formed with such molecules. At low supersaturations n_1 will be small and n_2 large, but since P_n increases with rising concentration, n_1 will also increase, whereas it is evident from equations 1 and 7 that n_2 will decrease. With increase of supersaturation, n_1 and n_2 will therefore approach one another, until the condition $n_1 = n_2$ is reached. Beyond this state n_1 will become greater than n_2, and nuclei formed by molecules of average energy will then appear. The "nucleus formation velocity" $\frac{dv}{dt}$ may be defined as the number of nuclei formed per second in unit volume; the part of $\frac{dv}{dt}$ corresponding with the nuclei considered will depend on P_n and on the range n_2 to n_1. Since all groups for which $n > n_2$ will condense, the relation may be expressed

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[2] The condition $W = 0$ does not correspond here with a true equilibrium between vapor and liquid. Once a drop of radius $\frac{3}{2} r$ is formed, it will grow indefinitely, since a decrease in free energy occurs in condensation on a surface of radius greater than r. The condition involved is different, therefore, according as the formation or growth of the drop is considered. Equilibrium between vapor and a surface actually formed holds when $x = r$.

$$\left(\frac{dv}{dt}\right)_{av} = \sum_{n = n_2}^{n = n_1} f(P_n) \tag{8}$$

This number includes all nuclei having from n_2 to n_1 molecules, but not nuclei of number less than n_1 (i.e., having radii between n and $\frac{3}{2} r$), formed by molecules of more than average energy. P_n and n_1 rise and n_2 falls with increasing concentration, and $\left(\frac{dv}{dt}\right)_{av}$ will increase rapidly with the supersaturation above the critical value. The optimum size of a nucleus will be that nearest the critical size, since on kinetic grounds the probability of formation increases as the size considered diminishes. The average size of a nucleus will therefore diminish as the concentration increases.

Nucleus growth

The growth of the nucleus depends on the rate of deposition of molecules on its surface and on the time spent in the condensation zone. The "specific velocity of growth" may be defined as $\frac{dm}{dt}$, where m is the mass of material deposited per unit area of surface. Now the number of molecules deposited per second on unit area is the difference between the number impinging on the surface and the number leaving it during this time. For a given solution pressure of the particle, therefore, $\frac{dm}{dt}$ will increase with the concentration of uncondensed molecules in the system. With a given supersaturation, $\frac{dm}{dt}$ will depend on the size of the particle, since the solution pressure increases as the radius diminishes.

If $\frac{dq}{dt}$ is the mass of material entering the condensation zone per second, V the volume of the zone, and μ_p the average size of a particle leaving the zone, then for equilibrium,

$$\frac{1}{v}\frac{dq}{dt} = \mu_p \frac{dv}{dt} \tag{9}$$

Let μ be the average mass of a nucleus, t_∞ the average time spent by a particle in the zone, and α the average area of the particle at any instant. Then we shall have ,

$$\mu_p = \mu + \int_0^{t_\infty} \alpha \frac{dm}{dt} dt \tag{10}$$

At the beginning of growth, $\frac{dm}{dt}$ will relate to the surface of the nucleus; since $\frac{dv}{db}$ and μ are fixed by the supersaturation, the initial value of $\frac{dm}{dt}$ for an average nucleus will be fixed also. The time t_∞ is determined by the relation of the path through the zone to the velocity of the particle. Hence as long as the conditions of injection are maintained, μ_p will be constant, i.e., successive "batches" of the dispersion will be similar.

Influence of pressure

In the emulsification method described, it is found experimentally that if the pressure of the vapor is raised and the cross-section of the jet is diminished in such a way as to keep $\frac{dq}{dt}$ constant, μ_p is reduced, so that by equation 9, $V\frac{dv}{dt}$ is increased. This means that on raising the pressure there must be an increase in either the volume of the zone or the equilibrium concentration, or (as probably happens) in both. An increase in concentration will reduce the average size of a nucleus but will increase the total mass of the nuclei formed per second; the diminution in μ_p therefore means a reduction in the time spent by a particle in the zone, in relation to the velocity of growth, i.e., an appropriate increase in the velocity of the particle relative to its path. Other things being equal, the velocity of the particle is determined by the entering linear velocity of the vapor, which is proportional directly to $\frac{dq}{dt}$ divided by the density of the vapor, and inversely to the cross-section of the jet. It may be concluded that for a constant value of $\frac{dq}{dt}$, with rising pressure the linear velocity of the vapor increases in relation to the depth of the condensation zone. This will mean a more efficient "sweeping" of the zone by the vapor, while the times spent in the zone by individual particles formed at different points will vary less; both these factors will tend towards greater homogeneity in the particle sizes, as actually observed. The zone will probably have approximately the form of a cone with the jet at the apex.

To a first approximation, the zone produced by the column of vapor entering the liquid may be regarded as the additive effect of a number of columns of smaller cross-section, i.e., with a given pressure the equilibrium will be practically independent of the cross-section of the jet. This was found to hold when the pressure was not too low. The above conclusions may be applied, therefore, to the influence of increasing pressure with a given jet, instead of with a fixed value of $\frac{dq}{dt}$.

Influence of soap concentration

Suppose that with fixed conditions of injection, $\frac{dm}{dt}$ is decreased. This means that in passing through the zone a particle will grow less than before, i.e., μ_p will be reduced. In order to maintain $\frac{dq}{dt}$ constant, $\frac{dv}{dt}$ must be increased, and conditions will therefore alter in such a way that this is effected. A given mass of the condensate will then comprise a larger number of smaller particles than before. The effect of an increasing concentration of sodium oleate in the aqueous phase of the emulsion may be ascribed to this phenomenon, since $\frac{dm}{dt}$ will be reduced progressively by addition of a surface-active colloid, through formation of a film round the particle which obstructs the access of further molecules. Now if the soap had no influence on $\frac{dv}{dt}$ at a given supersaturation of oil, the requisite increase in $\frac{dv}{dt}$ would necessitate a rise in the equilibrium supersaturation. It has been shown, however, that nucleus formation is conditioned by the interfacial tension, and since the latter is diminished by addition of soap, the reduction of $\frac{dm}{dt}$ is accompanied by a fall in the critical number of molecules, n_2. The range of group sizes available for nucleus formation by molecules of average energy is thereby extended, so that $\frac{dv}{dt}$ will rise independently of an increase in supersaturation. It does not follow that the latter will not take place, but the rise necessary will be less than if $\frac{dv}{dt}$ were independent of the soap concentration.

CONCLUSION

No claim is made for the experiments described, that they are exhaustive even over the limited field investigated, but the results obtained warrant the conclusion that an important new avenue of research has been opened. The study of emulsification by this new method is of interest in connection both with emulsions and with general condensation processes. An important feature of the work is quantitative specification of the experimental conditions and results.

SUMMARY

1. The possible means of preparing emulsions are discussed briefly in relation to the general methods of colloid chemistry, on the basis of the division into dispersion methods and condensation methods.

2. An experimental condensation method of preparing emulsions by injection of oil vapor into an aqueous liquid is described, and results obtained with the system benzene–sodium oleate solution are correlated on the basis of the particle size distribution, as determined by a sedimentation method. It is found that over the range of conditions investigated, the dispersion is independent of the vapor temperature, and of the cross-section of the jet if the pressure is not too low, but is made more homogeneous (without considerable alteration of the mean size) by increasing the pressure. Increase of the sodium oleate concentration effects a progressive shift in the range of particle sizes in a downward direction. The emulsions are reproducible and very homogeneous, practically the entire disperse phase lying between radius limits of which the higher is about twice the lower. Emulsions so formed are unstable if the initial soap concentration is low, but may be made more stable by the addition of more soap afterwards, and from the data it is concluded that the function exercised by the soap and emulsification is independent of its stabilizing action.

3. The mechanism of this process of emulsification is considered, and the experimental results are correlated by postulating the formation and growth of nuclei in the liquid phase.

In connection with the research, grateful acknowledgments are due to the following: The Department of Scientific and Industrial Research, for a Senior Research Award which enabled the work to be undertaken; Mr. D. C. Henry (Director of the Thomas Graham Colloid Research Laboratory in the University of Manchester), for laboratory facilities and for encouragement; Dr. W. Clayton, for his interest in the research and assistance in connection with publication.

REFERENCES

(1)(a) Clayton: The Theory of Emulsions, 2nd Edition. P. Blakiston's Son and Company, Philadelphia (1928).
(b) Clayton: J. Soc. Chem. Ind. (Chemistry & Industry) **51**, 129 (1932).
(2) Stamm and Kraemer: J. Phys. Chem. **30**, 992 (1926).
(3) Wood and Loomis: Phil. Mag. [7] **4**, 417 (1927).
Richards and Loomis: J. Am. Chem. Soc. **49**, 3086 (1927).
Richards: Ibid. **51**, 1724 (1929).
Freedman: British patent 332,533 (1930).
(3a) Bendixen: German patent 466,353 (1925).
(4) Lewis: Kolloid-Z. **4**, 211 (1909); Trans. Faraday Soc. **28**, 597 (1932).
(5) Roginsky and Shalnikoff: Kolloid-Z. **43**, 67 (1927).
(6) Nordlund: Kolloid-Z. **26**, 121 (1920).
(7) Gutbier: Z. anorg. Chem. **152**, 163; **155**, 199; **158**, 99 (1926).
(8) Kraemer and Stamm: J. Am. Chem. Soc. **46**, 2709 (1924).
(9) Lambert and Wightman: J. Optical Soc. Am. **11**, 393 (1925).
(10) Sumner: Trans. Faraday Soc. **28**, 20 (1932).

(11) Sumner: J. Sci. Instruments **7**, 398 (1930).
(12) Harkins and Beeman: J. Am. Chem. Soc. **51**, 1674 (1929).
(13) Plateau: Statique des Liquides, Vol. II, pp. 209, 254 (1873).
(14) Thomson, W.: Phil. Mag. [4] **42**, 448 (1871).
(15) Volmer and Weber: Z. physik Chem. **119**, 277 (1926).
(16) Farkas: Z. physik. Chem. **125**, 236 (1927).
(17) Ostwald: Z. physik. Chem. **34**, 495 (1900).
Hulett: Z. physik. Chem. **37**, 385 (1901).

THE FUSION CURVES FOR THE SYSTEMS AMMONIA-PROPYL ALCOHOLS AND AMMONIA-BUTYL ALCOHOLS

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INTRODUCTION

Baume and Perrot (1) used the phase law method to investigate the system methyl alcohol–ammonia. Broderson (2) used the same method with the system ethyl alcohol–ammonia. Baume and Perrot found that the compound $CH_3OH \cdot NH_3$ was formed in the ammonia–methyl alcohol system. Broderson found the compounds formed in the ammonia–ethyl alcohol system to be $C_2H_5OH \cdot NH_3$ and $2(C_2H_5OH) \cdot NH_3$.

The object of this work was to apply the phase law method to systems of ammonia and some of the other alcohols of this series.

APPARATUS

The melting points were determined using a nickel–iron thermocouple, the potential differences being measured with a potentiometer.

The thermocouple was constructed by joining the junctions with bronze solder. The copper–nickel and the copper–iron junctions were kept surrounded by chipped ice from which the water drained away. The nickel–iron junction was placed in the melting point apparatus.

Calibration of the thermocouple

Table 1 gives the data used in plotting a curve from which melting points in degrees centigrade were read.

Melting point tube

The melting point tube used is shown in figure 1. The samples of alcohol and ammonia were introduced through A. C is a constriction in the glass tubing. The glass rod D carried a short piece of rubber tubing, B, at the lower end. The rod D has a constriction underneath the rubber tubing B, so that the tubing is held in place by means of a platinum wire wrapped around the tubing just over the constriction in the glass rod.

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[1] From a thesis submitted by Ethel Ann Jones to the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The rod D was held in place at the upper end at E by a short piece of rubber tubing. When the rod was raised the rubber tubing at B closed the melting point tube at the constriction C.

F is a glass tube, closed at the lower end, and sealed into the larger tube. The small tube F was used to carry the thermocouple to the lower end of the melting point tube. G is a hollow cylinder of iron with coils of steel wire attached at H and H′.

These steel coils served two purposes: first, to stir the ammonia alcohol system, and second, to break the rise and fall of the iron cylinder, thus protecting the glass tube.

Method of stirring the alcohol–ammonia systems

The melting point tube carrying the iron cylinder and coils was slipped through a coil made from a large number of turns of copper wire carrying an intermittent D. C. current which alternately magnetized and demagnetized the iron cylinder, causing it to move upward and downward, resulting in the coil H stirring the system in the lower part of the melting point tube.

TABLE 1

Calibration of thermocouple

CALIBRATING SUBSTANCES	POTENTIOMETER READINGS	TEMPERATURE
	volts	*degrees C*
Ammonia	0.001033	b.p. −33.4
Chlorobenzene	0.001412	f.p. −45.2
Chloroform	0.001955	f.p. −63.5
Ammonia	0.002362	f.p. −78
Carbon dioxide (solid)	0.002405	s.p. −78.92
Carbon disulfide	0.003252	f.p. −111.6
Ethyl ether	0.003552	f.p. −116.3

The D. C. current was made intermittent by a motor-driven interrupter making contacts at intervals of about one per second. Contact was about one-tenth of a second in duration.

In figure 2, J is a large test tube. L is a tube ending under mercury at Q with water above the mercury. The tube L takes care of any excess pressure developed in J. The tube K connects J with the melting point apparatus M through a short rubber connection at X. O is a Dewar flask containing liquid air. The Dewar flask was supported in a glass cylinder with cotton plugs holding it in place

MATERIALS

The liquid ammonia used was dried by distilling from contact with sodium. The alcohols were of Eastman grade dried with metallic calcium

METHOD

The melting point tube M, figure 2, was cleaned by connecting as shown in figure 2 with the valve at B pushed down. The test tube J contained liquid ammonia in contact with sodium. The melting point tube M was about one half immersed in liquid air, resulting in ammonia condensing in M. When about 20 cc. of ammonia had distilled into the tube, the connection at X was broken. The rubber tubing was left on the tube K and was closed with a screw clamp S. The melting point tube M was then removed from the liquid air and the ammonia allowed to melt. The liquid ammonia passed rapidly out of the tube A on inversion of the melting point tube. The above procedure was repeated three times. The melting point tube was then connected at A to the vacuum pump. After several minutes the

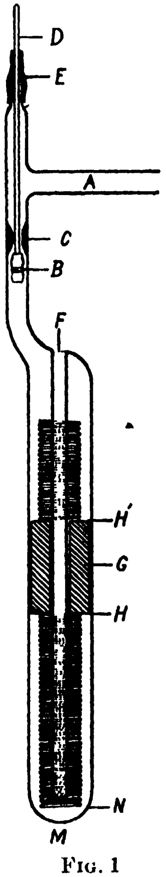


Fig. 1

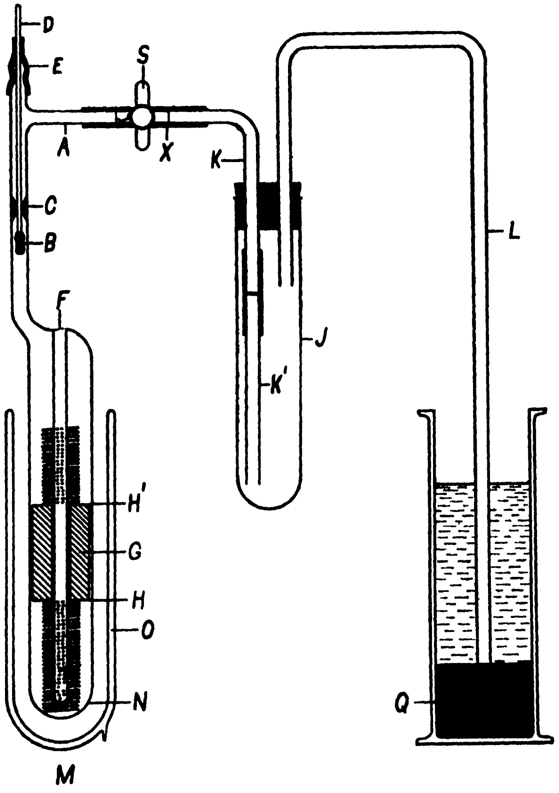


Fig. 2

Fig. 1. Melting Point Tube

Fig. 2. Apparatus for Melting Point Determinations

tube was closed at A with a rubber tube and screw clamp, disconnected from the vacuum pump, and weighed. All weighings were made in a silvered Dewar flask. The melting point tube M was then evacuated again *and connected as shown in figure 2 to a clean test tube J containing the sample* of alcohol to be introduced into M. On opening the screw clamp S the alcohol flowed up through K′ and K into M. The tube K′ was used only when alcohol was being transferred from J to M. A rubber tube and screw clamp was then placed on A and the melting point tube M, containing the alcohol, was weighed, and then connected again to the test tube J containing liquid ammonia in contact with sodium. After the desired quantity of ammonia had distilled into M, the valve B was closed and the melting point tube M was allowed to stand above a small quantity of liquid air in the Dewar flask, so that the ammonia melted from the upper surface downward and before the alcohol; this was done in order to prevent the melting of the alcohol first with its resulting expansion causing breaks in the melting point tube at F and N. After the ammonia and alcohol had melted, the melting point tube was placed in the magnetizing coil, the thermocouple was introduced into the small tube at F, and a melting point determination made as follows. The potentiometer was balanced against a standard cell so that a spot of light reflecting from a galvanometer mirror rested on zero of a scale. A switch was then turned bringing the thermocouple into the potentiometer circuit. The motor for breaking the D. C. current was then started, resulting in the thorough stirring of the solution as it was cooled with liquid air. As soon as the solution was partly solidified the flask of liquid air was lowered and the temperature of the mixture allowed to rise slowly. When only a few crystals remained in the thoroughly stirred solution the potentiometer was balanced, read, and the above procedure repeated. The melting point tube was then prepared for weighing again so that the weight of ammonia in the system could be calculated.

RESULTS

Measurements of molecular percentage compositions and freezing points were made with the results given in tables 2 to 7 (see figures 3 to 8).

Normal propyl alcohol did not crystallize but solidified as a clear glass. Mixtures of the alcohol and small quantities of ammonia also gave glasses. At 21.74 mole per cent of ammonia distinct crystallization occurred.

The fusion curve for the system normal propyl alcohol–ammonia indicates: (1) There is formed one compound of ammonia and normal propyl alcohol, composed of one mole of ammonia and one mole of alcohol. The melting point is about −77.1°C. (2) The compound formed is relatively slightly dissociated into ammonia and the alcohol, since the change in direction of the curve at its maximum point is sharp. (3) One eutectic is distinctly indicated at about −90°C., having a composition of 73.5 mole

TABLE 2

Data for the fusion curve of ammonia and normal propyl alcohol

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C		*degrees C.*
0 0	−127 1 (not definite)	66 95	−86 2
21 74	−99 0	68 73	−87 1
29 39	−91 0	70 79	−88 6
31 39	−88 8	72 42	−89 3
36 69	−83 7	75 55	−88 2
37 8	−82 8	77 29	−87 0
42 37	−79 3	78 3	−86 7
44 65	−79 0	79 32	−85 7
46 21	−78 2	83 18	−83 5
49 66	−77 1	85 12	−82 6
50 73	−77 1	89 66	−81 1
51 66	−77 3	95 54	−79 1
53 58	−78 0	96 12	−78 9
55 12	−79 6	97 17	−78 1
56 15	−80 1	99 25	−77 5
60 89	−81 4	100 00	−77 4
63 3	−84 5		
65 67	−85 1		

TABLE 3

Data for the fusion curve of ammonia and isopropyl alcohol

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C		*degrees C*
0 0	−86 6	64 25	−74 0
0 31	−87 4	68 51	−75 5
13 82	Glass	72 19	−77 8
21 82	−88 1	73 57	−79 1
27 11	−85 0	76 97	−82 1
36 75	−81 1	80 55	−85 1
43 33	−76 3	82 6	−85 6
46 79	−73 9	87 07	−85 2
48 66	−72 8	88 06	−84 8
49 98	−72 0	89 16	−83 6
50 98	−71 9	91 28	−83 0
54 28	−71 9	92 78	−82 0
56 60	−71 9	97 87	−79 7
59 16	−72 2	98 51	−78 8
60 62	−72 9	100 00	−77 4
61 84	−72 9		

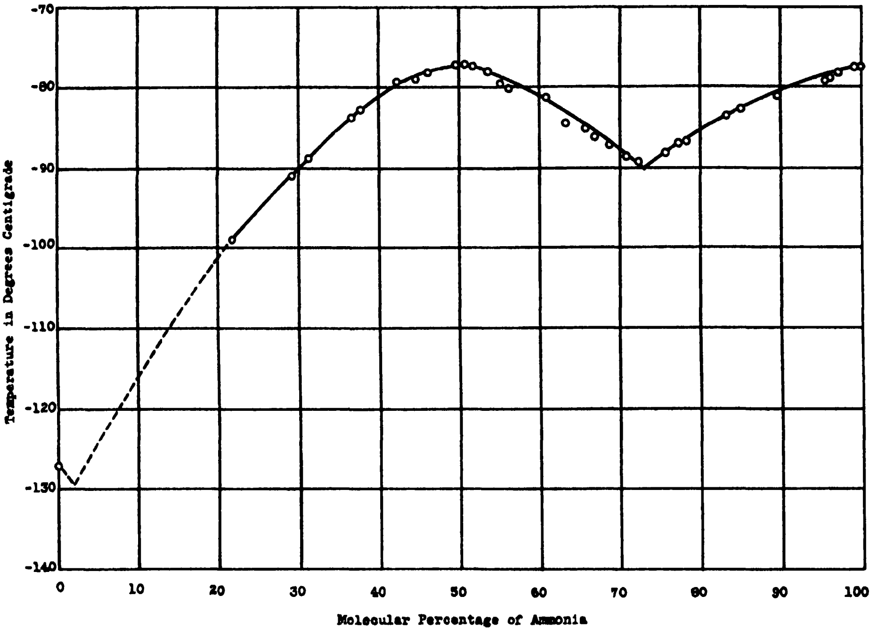


FIG. 3. AMMONIA-*n*-PROPYL ALCOHOL

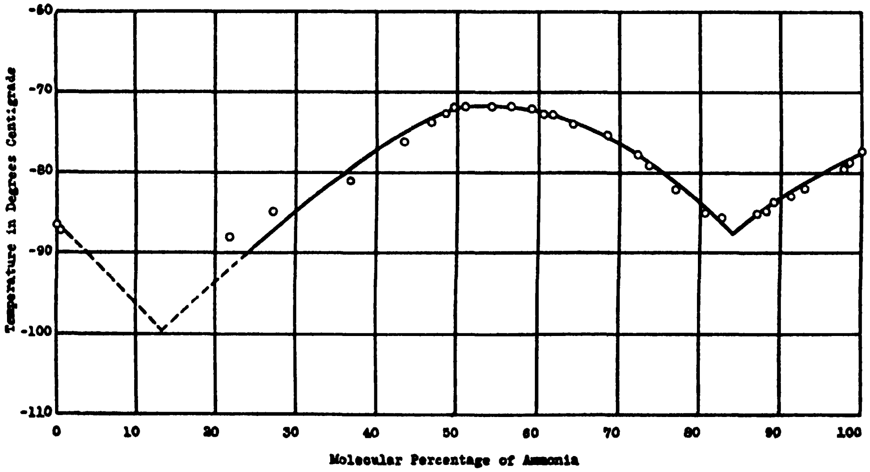


FIG. 4. AMMONIA-ISOPROPYL ALCOHOL

per cent of ammonia. There is probably another one below −127°C., which could be definitely located if the system could be made to crystallize in this region.

The fusion curve for the system ammonia-isopropyl alcohol indicates:

(1) There is one compound of ammonia and isopropyl alcohol formed, composed of one mole of ammonia and one mole of the alcohol. The melting point of the compound is about −71.9°C. (2) The compound is relatively more dissociated than the one in the ammonia-normal propyl alcohol system. This is indicated by the flattened portion of the curve at its maximum. (3) There are two eutectic mixtures, one in the region having the composition between zero mole per cent of ammonia to 21.82 mole per cent and below −87°C. Owing to the formation of a glass this eutectic could not be definitely located. The other eutectic was in the region of 85 mole per cent of ammonia and at about −86°C.

TABLE 4

Data for the fusion curve for the ammonia-normal butyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0 00	−90 4	67 31	−66 7
1 8	−91 9	69 32	−67.7
13 95	−80 6	71 22	−68.4
15 66	−77.4	74 08	−68.9
17.69	−74 2	77 4	−71 8
22.70	−72 8	78 05	−71.6
29.56	−69.4	80 31	−72 7
32 53	−66 6	83 12	−72 9
39 38	−61 9	83 42	−72.6
39 98	−62.3	86 95	−75.2
43 77	−61.3	89 7	−76.6
47.62	−60 1	91 76	−77.1
50.44	−60 2	93 16	−77.3
52 24	−60 6	95 5	−77.5
56 43	−62 0	96 16	−78.2
57.53	62 1	96 7	−78.3
59 59	−63 1	97.0	−78.4
62 51	−63 6	100 0	−77.4

The fusion curve for the system ammonia-normal butyl alcohol indicates: (1) There is one compound of ammonia and normal butyl alcohol formed. It is composed of one mole of ammonia and one mole of normal butyl alcohol and melts at about −60°C. (2) The compound formed is but relatively slightly dissociated, this is indicated by the fact that the curve is relatively sharp at the maximum. (3) There are two eutectic mixtures indicated, one in the region having the composition between 1 mole per cent of ammonia and 13.95 mole per cent and below −90.4°C. The other one is in the region having a composition of about 97 mole per cent of ammonia and a temperature of −78.4°C.

The fusion curve for the system ammonia–isobutyl alcohol indicates: (1) There is one compound of ammonia and isobutyl alcohol formed. It is composed of one mole of ammonia and one mole of isobutyl alcohol, and melts at −59.1°C. (2) The compound formed is but slightly dissociated, since the curve is relatively sharp at the maximum. (3) The pure isobutyl alcohol solidifies forming a glass so that the composition and temperature for the eutectic mixture in the region of 100 mole per cent alcohol was not determined. On the other hand, in the region of 97 mole per cent of ammonia a eutectic mixture formed at −78.5°C.

TABLE 5

Data for the fusion curve for the ammonia–isobutyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.00	−108.0	64.85	−66.4
	value given in	66.32	−67.0
	critical tables	69.37	−68.4
12.52	−83 4	71.39	−68.9
17.17	−78 1	71.42	−69.4
27.92	−71.2	73.63	−71.2
30.88	−68.1	76.5	−72.3
37.16	−65.0	78.61	−73.2
39.57	−62.6	80.42	−74.6
43.25	−59.6	81.25	−74.9
43.63	−60.0	82.84	−76.0
46.07	−59.6	84.2	−76.0
48.16	−59.3	86.92	−77.5
50.13	−59.1	90.96	−77.3
51.12	−60.2	92.2	−77.9
51.89	−59.5	93.77	−78.6
54.91	−61.6	95.21	−78.2
55.05	−60.3	95.85	−78.1
57.44	−62.9	96.28	−78.5
61.62	−64.3	97.29	−78.5
64.06	−65.4	100.00	−77.4

The fusion curve for the system ammonia–*secondary* butyl alcohol indicates: (1) There is one compound of ammonia and *secondary* butyl alcohol formed, composed of one mole of ammonia and one mole of the alcohol. Its melting point is −60°C. (2) The compound formed is but relatively slightly dissociated, since the curve is relatively sharp at its maximum. (3) There are two eutectic mixtures possible but, since the alcohol solidified to a glass at −114.7°C. and did not give crystals until about 13 moles per cent of ammonia were added, the exact composition of this eutectic was not determined. The other eutectic is in the region of about 97 mole per cent of ammonia and about −79°C.

The fusion curve for the system ammonia-*tertiary* butyl alcohol indicates: (1) There is one compound of ammonia and *tertiary* butyl alcohol formed,

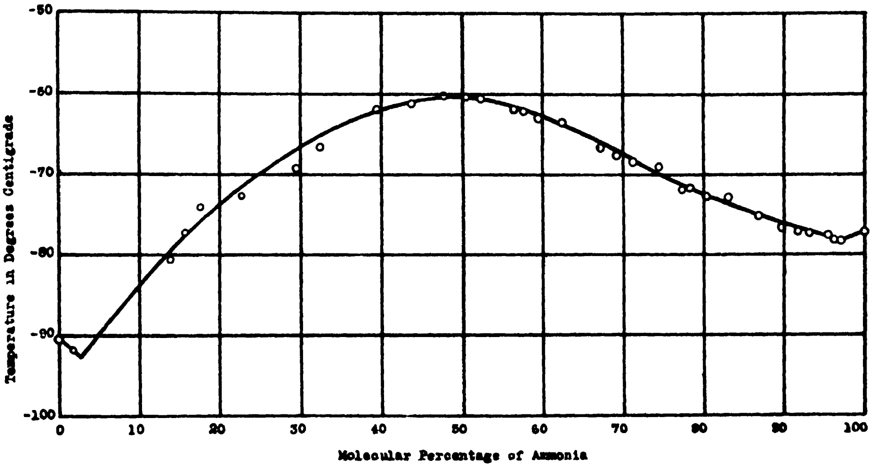


Fig. 5. Ammonia-*n*-Butyl Alcohol

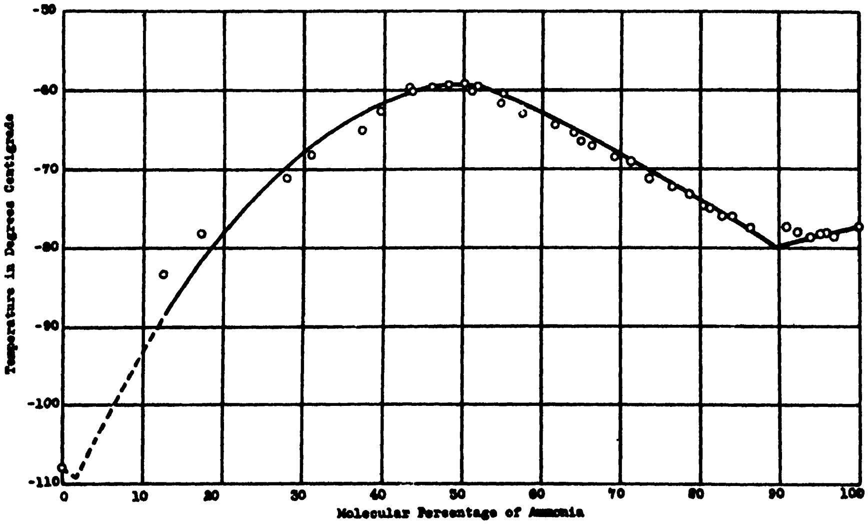


Fig. 6. Ammonia-Isobutyl Alcohol

composed of one mole of alcohol and one mole of ammonia, and melting at −43.9°C. (2) The compound formed is relatively more dissociated than the compound formed between ammonia and the other butyl alcohols.

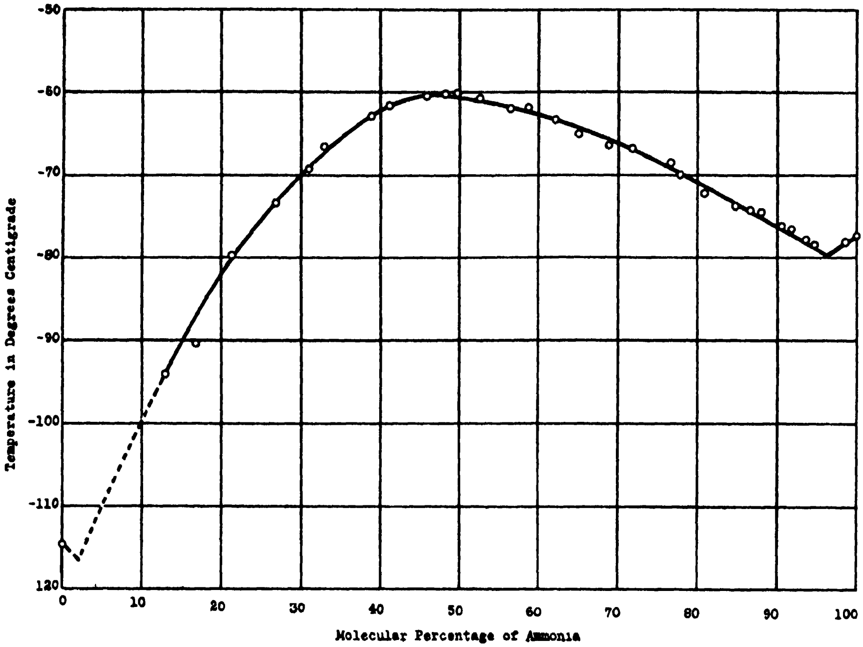


FIG. 7. AMMONIA-*secondary* BUTYL ALCOHOL

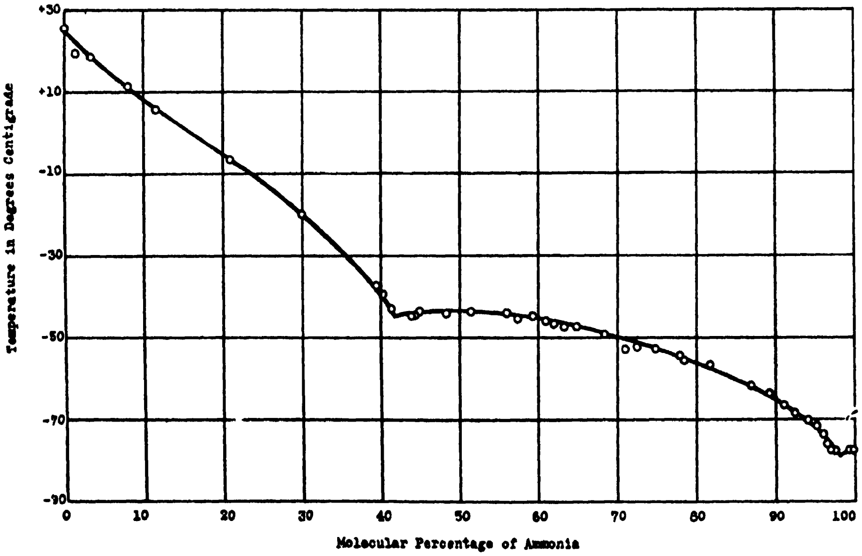


FIG. 8. AMMONIA-*tertiary* BUTYL ALCOHOL

TABLE 6

Data for the fusion curve for the ammonia–secondary butyl alcohol system

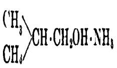
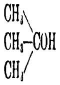
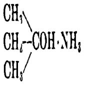
MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C		*degrees C*
0 0	−114 7	62 17	−63 3
13 0	−94 2	68 86	−66 4
16 78	−90 4	71 83	−66 9
21 36	−79 9	76 63	−68 6
26 91	−73 4	77 86	−70 0
30 95	−69 4	80 93	−72 1
32 9	−66 6	84 91	−73 6
38 94	−62 8	86 63	−74 2
41 06	−61 7	88 23	−74 4
45 72	−60 5	90 61	−76 1
48 19	−60 2	91 87	−76 5
49 83	−60 1	93 69	−77 9
52 63	−60 7	94 73	−78 5
56 43	−62 0	98 67	−78 1
58 62	−61 9	100 00	−77 4

TABLE 7

Data for the fusion curve for the ammonia–tertiary butyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C		*degrees C*
0 0	25 7	63 22	−47 4
1 3	19 6	64 93	−47 3
3 33	18 8	68 45	−49 5
8 01	11 1	70 93	−53 0
11 53	5 9	72 39	−52 3
20 81	−6 7	74 85	−52 7
29 98	−20 1	77 88	−54 5
39 45	−37 6	78 53	−55 9
40 19	−39 6	81 77	−56 5
41 31	−43 0	87 04	−61 7
43 98	−44 8	89 31	−63 7
44 4	−44 7	91 08	−66 7
44 99	−43 3	92 34	−68 5
48 45	−44 3	94 09	−69 9
51 47	−43 9	95 15	−71 8
55 93	−44 2	96 02	−73 6
56 13	−44 1	96 45	−76 0
57 37	−45 5	96 84	−77
59 3	−44 8	97 49	−77 5
60 92	−46 1	99 12	−77 1
62 04	−46 9	100 00	−77 4

TABLE 8

OBSERVER	AMMONIA MELTING POINT	ALCOHOLS				COMPOUNDS			EUTECTICS			
		Composition	Melting point	Melting point in Critical Tables	Type of solid	Composition	Melting point	Qualitative indication of dissociation	Composition	Melting point	Composition	Melting point
	degrees C		*degrees C*	*degrees C*			*degrees C*			*degrees C.*		*degrees C*
Jones	−77 4	Normal propyl alcohol $CH_3\cdot CH_2\cdot CH_2OH$	−127 1	−127	Glass (1)	$CH_3\cdot CH_2\cdot CH_2OH\cdot NH_3$	−77 1	Relatively slight	Less than 21.74 mole per cent ammonia	Less than −127	73.5 mole per cent ammonia	90
Jones	−77 4	Isopropyl alcohol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$	−86 6	−85 8	Crystals	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH\cdot NH_3$	−71 9	More than in the preceding case	Less than 21.82 mole per cent ammonia	Below −87	85 0 mole per cent ammonia	−86
Jones	−77 4	Normal butyl alcohol $CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$	−90 4	−89 8	Crystals	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH\cdot NH_3$	−60	Relatively slight	Less than 13.95 mole per cent ammonia	Below −90 4	97 mole per cent ammonia	−78 4
Jones	−77 4	Isobutyl alcohol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\ CH_2OH$	−108	−108	Glass (1)	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CH_2OH\cdot NH_3$	−59 1	Relatively slight	Less than 12 52 mole per cent ammonia	Below −108	97 mole per cent ammonia	−78 5
Jones	−77 4	*secondary* Butyl alcohol $CH_3\cdot CH_2\cdot CHOH\cdot CH_3$	−114 7	Not given	Glass	$CH_3\cdot CH_2\cdot CHOH\cdot CH_3\cdot NH_3$	−60	Relatively slight	Less than 13 mole per cent ammonia	Below −114 7	97 mole per cent ammonia	−79
Jones	−77 4	*tertiary* Butyl alcohol  $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$	25 7	25 5	Crystals	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH\cdot NH_3$	−43 9	Relatively high	42 5 mole per cent ammonia	−43	97 mole per cent ammonia	−77 5
Baume and Perrot (2)		Methyl alcohol CH_3OH		−97 8		$CH_3OH\cdot NH_3$	+55	Relatively slight				
Broderson (3)	−76 5	Ethyl alcohol C_2H_5OH	−112	−117 3		$C_2H_5OH\cdot NH_3$ $(C_2H_5OH)_2NH_3$ Transition point −89 5°C.	−74 2	Relatively slight				
Briner and Agathon (4)		Phenol C_6H_5OH		41		$C_6H_5OH\cdot NH_3$	Near 0	Relatively high	36 mole per cent ammonia	0	65 mole per cent ammonia	−20

(1) Gazz. chim. ital. **33**, 331-43 (1903).

(2) Baume and Perrot: Compt. rend. **151**, 528 (1910).

(3) Broderson: The Fusion Curve of Ammonia and Ethyl Alcohol. Master's thesis, University of Kansas, 1911.

(4) Briner and Agathon: Helv. Chim. Acta **9**, 905 (1926).

(3) Two eutectic mixtures are indicated; one having a composition of about 42.5 mole per cent of ammonia and melting at about −43°C., the other at about 97 mole per cent of ammonia and melting at −77.5°C.

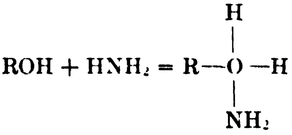
These data are summarized in tables 8 and 9.

DISCUSSION

There are two possibilities to be considered in attempting to explain the mechanism of addition reactions between oxygen compounds and nitrogen compounds. In the systems of anhydrous ammonia and alcohols described by the fusion curves previously given, the question is whether the compounds are formed by ammonia adding to the oxygen of the alcohol as represented by this general reaction:

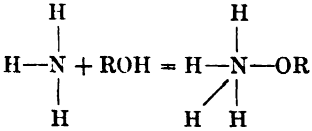
TABLE 9

ALCOHOL		MELTING POINT OF ALCOHOL	MELTING POINT OF COMPOUND	T(50 MOLE PER CENT AMMONIA) − T(55 MOLE PER CENT AMMONIA)	QUALITATIVE INDICATION OF DISSOCIATION OF COMPOUND
		degrees C	*degrees C*		
Primary	Propyl	−127	−77.1	1.4	Relatively slight
	Butyl	−89.8	−60	1.3	Relatively slight
	Isobutyl	−108	−59.1	1.9	Relatively slight
Secondary	Isobutyl	−85.8	−71.9	0.1	Relatively more than in preceding case
	secondary Butyl	−114.7	−60	0.8	Relatively more than in preceding case
Tertiary	*tertiary* Butyl	25.5	−43.9	Less than 0.1	Relatively high



$$ROH + HNH_2 = R{-}\overset{\displaystyle H}{\underset{\displaystyle NH_2}{O}}{-}H$$

or whether the alcohol adds to the nitrogen of the ammonia in this manner:



$$H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}} + ROH = H{-}\overset{\displaystyle H}{\underset{\displaystyle H\ H}{N}}{-}OR$$

It has been thought by several workers (3) in the field that compounds are formed between a number of types of oxygen compounds such as alcohols, ethers, aldehydes, ketones, and acids combining with both organic and inorganic acids.

The oxonium theory attempts to explain the mechanism of compound formation in these cases by considering that combination may be due to the basic properties of oxygen. The ending "onium" indicates basic properties. Many oxygen reactions can be explained if the valence of oxygen is considered greater than two.

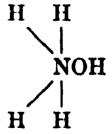
Elements near oxygen in the periodic system show basic properties, for example, iodine in phenyl iodide is able to add another mole of phenyl iodide forming diphenyl iodonium iodide, which on being treated with silver hydroxide gives diphenyl iodonium hydroxide, a strong base. Sulfur gives a basic substance in the compound $(CH_3)_3SOH$. These facts help support the oxonium theory by indicating that the elements near oxygen in the periodic table show basic properties.

In the systems studied, consisting of alcohols and anhydrous ammonia, we have in the alcohols oxygen which may function as oxonium oxygen and in the ammonia nitrogen which may react as ammonium nitrogen.

Ammonia (4) in some cases behaves as a saturated substance, since it does not combine with more hydrogen to form NH_4 or NH_5. In some cases it shows unsaturated properties, in that it combines directly with water to form ammonium hydroxide.

Rupert (5) shows that ammonia forms with water two compounds both freezing at −79°C. One compound is formed by the addition of one mole of ammonia and one mole of water. The properties of a solution of ammonia in water indicate that these properties would be represented by a substance having the formula NH_4OH. This compound could be considered to be formed in this manner:

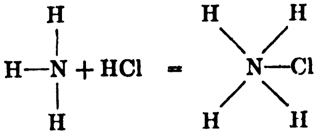
$$NH_3 + H^+ + OH^- = (NH_3)H^+ + OH^- = NH_4OH \;=$$



Rupert's second compound has the composition, $2NH_3 \cdot H_2O$ or $(NH_4)_2O$ and could be called ammonium oxide. Addition in this compound can be represented as follows:

$$NH_3 + HOH + NH_3 = NH_4ONH_4$$

Ammonia (4) also combines with hydrochloric or other acids to form salts.

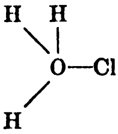


In this type of reaction ammonia is able to add only pairs of unlike atoms or groups which show a contrast to each other. It is not able to add a pair of chlorine atoms or a pair of hydrogen atoms. One of the characteristics of this type of valence change is that one of the atoms or groups added is always capable of splitting off as a negative ion, leaving the other atom or group as a part of the positive ion. Another characteristic property is the fact that the addition reaction can be easily reversed. In the case of ammonium hydroxide the reversal to ammonia and water takes place so readily that it is impossible to isolate the ammonium hydroxide above −79°C.

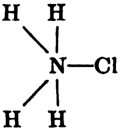
In the case of ammonium chloride the union is much more stable and dissociation into ammonia and hydrogen chloride takes place appreciably only at higher temperatures.

This type of valence change shown by nitrogen in ammonia compounds is not generally shown by other elements, but is definitely shown by several members of the nitrogen family, also by oxygen, sulfur, and iodine.

Water forms with hydrogen chloride three (6) unstable hydrates. The monohydrate may be indicated as



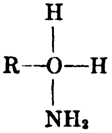
This is analogous to the formula for ammonium chloride



The hydrate of hydrogen chloride is much more easily decomposed than is ammonium chloride. It may be that the only difference between the unsaturation shown by ammonia and the unsaturation shown by water is in the degree of stability of the products. That is, the salts formed by the action of acids and ammonia are stable and form an important class of compounds. But the products formed by the addition of acids to water and similar oxygen compounds are so unstable that they have been neglected.

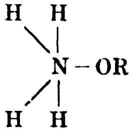
Combinations formed then by additions to ammonia are called ammonium compounds; the corresponding oxygen compounds which are much less stable are known as oxonium compounds. Other substances which show similar properties are known as phosphonium, arsonium, stibonium, sulfonium, and iodonium compounds. As a group they are referred to as "oxonium" compounds. All have the general characteristics shown by the ammonium compounds in that: (1) they are formed by the addition of a positive and a negative group to some compound; (2) one of the groups added breaks off as a negative ion; (3) the addition products are unstable and may dissociate again into two definite compounds.

In order to prove the type of addition of alcohols with anhydrous ammonia some of the properties of the compounds would have to be determined in order to decide whether the compounds are of the general type

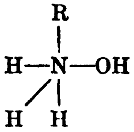


$$\begin{array}{c} H \\ | \\ R{-}O{-}H \\ | \\ NH_2 \end{array}$$

or



or possibly,



The primary alcohols resemble each other in properties more than they resemble either the secondary or tertiary alcohols, that is, each member of a class resembles other members of the same class. Therefore, it is not surprising to find some differences in the relative dissociation of the alcohol ammonia compounds formed with the three classes of alcohols. As shown in table 9, the relative dissociation of the compounds formed between anhydrous ammonia and the primary, secondary, and tertiary alcohols used in these studies is in the following order: primary alcohols–ammonia, relatively slight dissociation; secondary alcohols–ammonia, slightly more dissociated; tertiary alcohols–ammonia, dissociation relatively high.

SUMMARY

1. The fusion curves for systems of ammonia–propyl alcohols and ammonia–butyl alcohols, together with similar curves previously obtained for the systems ammonia–methyl alcohol and ammonia–phenol, indicate very definitely the formation of a compound in each case consisting of one mole of the alcohol and one mole of ammonia, each compound having a congruent melting point.

2. The curve for the ammonia–ethyl alcohol system indicates definitely a compound $C_2H_5OH \cdot NH_3$ with a congruent melting point and seems to indicate another $(C_2H_5OH)_2 \cdot NH_3$(2), but this was not definitely determined.

3. The fusion curves for the systems ammonia–*tertiary* butyl alcohol and ammonia–phenol are not as smooth as the others. At some places it cannot be definitely stated whether other compounds are indicated.

4. The dissociation of the ammonia–alcohol compounds formed is in the order: primary alcohol–ammonia, relatively undissociated; secondary alcohol–ammonia, slightly more dissociated; tertiary alcohol–ammonia, relatively highly dissociated.

5. A value for the melting point of *secondary* butyl alcohol was not found in the literature. The melting point as determined by the method used in this work is −114.7°C.

6. The ammonia–alcohol compounds may be oxonium or ammonium complexes.

REFERENCES

(1) Baume and Perrot: Compt. rend. **151**, 528 (1910).
(2) Broderson: The Fusion Curve of Ammonia and Ethyl Alcohol. Master's thesis, University of Kansas, 1911.
(3) Collie and Tickle: J. Chem. Soc. **75**, 710 (1899).
Kendall: J. Am. Chem. Soc. **36**, 1222, 1722–34 (1914); **37**, 149 (1915).
Maass and McIntosh: J. Am. Chem. Soc. **34**, 1273–90 (1912); **35**, 535 (1913).
(4) Williams, R. J.: Introduction to Organic Chemistry. D. Van Nostrand Co., New York (1928).
(5) Rupert: J. Am. Chem. Soc. **31**, 866 (1909).
(6) Rupert: J. Am. Chem. Soc. **31**, 851 (1909).

STUDIES ON SILICIC ACID GELS. III

The Effect of the Addition of Some Solutes on the Time of Set

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INTRODUCTION

The setting of a gel of hydrated silica, or a silicic acid gel as it is commonly called, is affected, among other things, by the concentrations of the solutions, the type of silicate, the temperature, the pH of the mixture, and the presence of additional soluble materials. Several investigations are being conducted in this laboratory upon the effects of some of these factors upon the time of set. In connection with a study of the effect of the pH of the mixture, the idea suggested itself that measurements be made upon the pH of mixtures containing certain additional solutes such as ammonia, the amines, pyridine, and certain others.

In this paper are presented some of our typical results. The effect of the change in the pH of the mixture and the specific effects of certain substances are shown. An attempt has been made to explain certain of these results.

The gel mixtures were prepared by mixing solutions of sodium silicate with dilute acetic acid. Such a process produces in the mixture sodium acetate together with excess acetic acid. A possible, though not practicable, way of avoiding the presence of these soluble materials has already been pointed out by Hurd and Letteron (1), that is, to start with a pure suspension of colloidal silicic acid in water. The results of Werner (2) and Kröger (3) show that the removal of the last traces of electrolytes is impossible. It is also obviously impossible to determine the time of set correctly.

The results of various studies reported in the literature on the effects of added materials on the time of set of the gel are difficult to interpret, because in general the specific effect of the solute has not been distinguished from the indirect effect due to a change in the pH of the mixture. We may mention here only a few of the results reported.

The addition of strong bases has been found to prevent the formation of a gel, in fact, solutions of sodium hydroxide will peptize an already formed silicic acid gel. The effect of weak bases is less pronounced than that of strong bases. The effect of ammonia was studied by Bhatnagar and Mathur (4). Various compounds, including ammonia and pyridine, were studied by Prasad and Hattiangadi (5). The latter determined the pH of their mixtures. These compounds were found to accelerate setting.

The effect of excess acid has been considered by many workers. We may mention Holmes (6), Prasad and Hattiangadi (7), Maschke (8), and Pappada (9). Excess acid has been found to increase the time of set, although Holmes, and later Hurd and Letteron, have shown that at high acid concentrations the time of set decreases rapidly, until at very high acid concentrations sodium silicate solutions cannot be mixed with the acid to give a clear solution.

The effect of salts on the time of set has been considered by a number of workers, including Prasad and Hattiangadi, Pappada, and Werner.

The effects of various unionized solutes have been studied, among them the alcohols, studied by Prasad and Hattiangadi, and certain gums and sugars, investigated by Wulf and Praetorius (10).

The general impression received from a survey of the literature is that the addition of bases to an acid gel mixture hastens the setting and that excess acids retard the setting. The effects of other solutes have not in general been divided into their effect on the pH of the mixtures and their specific effects.

EXPERIMENTAL

The determination of the pH in colloidal solutions has been the subject of much study and of voluminous discussion. The system under investigation here involves a colloidal material, namely colloidal silicic acid. In similar systems Prasad and Hattiangadi (7) have measured the pH by means of an indicator method. They note in their discussion, however, that the turbidity of the gel mixture caused difficulty in determining the color of the indicator, and also that the alcoholic solution affected the setting of the gel.

A study of the various methods has led us to the belief that the quinhydrone method would prove the most applicable, especially since no alkaline gels were to be studied. A study of gels formed from alkaline mixtures has led us to believe that such gels differ considerably from the gels produced from acid mixtures. We have, accordingly, limited our study to acid gels.

A series of determinations of the pH of gel-forming mixtures from the time of mixing until after the time of set, using the quinhydrone method,[1] has shown that only a negligible change, if any, in the pH of typical acid mixtures of various sodium silicate solutions with excess acetic acid occurs from the time of mixing until after the gel has set. As a further check on the quinhydrone method, comparisons were made of the pH values obtained on portions of the same mixture by the quinhydrone method and by the use of a special glass electrode-vacuum tube potentiometer circuit, using a McInnes and Dole electrode.[2] The agreement was within the limits of experimental error. No doubt there is a possibility that the quinhydrone may have a specific effect on the time of set. The time of set and the pH were accordingly determined on portions of the same mixture, no quinhydrone having been added to the portion upon which the time of set was determined.

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[1] These experiments were performed by Mr. D. P. Roehm at Union College in 1931–1932.

The time of set was determined as follows. The correct amounts of solutions were drawn from bottles which had been standing for at least several hours in a water thermostat. They were mixed in a 100-cc. Pyrex Griffin beaker which was standing in the thermostat. The time of set was determined by the tilted rod method described by Hurd and Letteron (1). The method consists of inserting a small stirring rod into the gel at an angle of about 20° to the vertical until the gel is stiff enough to hold the rod in its tilted position. The glass rod is about 3 mm. in diameter and about 8 cm. long, drawn out to a stubby point and fire-polished.

The effects of ammonium hydroxide, of methyl-, dimethyl-, and trimethylamines, of pyridine, and of aniline were studied. The sodium silicate was "E" brand, Philadelphia Quartz Company silicate.[3] It was diluted with distilled water. The concentration was determined by titration with standard sulfuric acid using methyl orange, giving the sodium hydroxide equivalent. From this and the soda–silica ratio supplied by the maker, the concentration in equivalents of sodium hydroxide and gram-moles of silica per liter were calculated. The acetic acid was prepared from J. T. Baker C.P. acetic acid by dilution with distilled water. Its strength was determined by titration with standard sodium hydroxide, using phenolphthalein as an indicator.

The ammonium hydroxide was prepared by diluting Grasselli C.P. ammonium hydroxide (sp. gr. 90). The methylamine was prepared and purified in our laboratory. The other amines were purchased from the Eastman Kodak Company, the dimethylamine in the form of the hydrochloride. This amine was set free by distillation from a solution of the hydrochloride with excess sodium hydroxide. The strengths of the diluted ammonium hydroxide and the amine solutions were determined by titration with standard sulfuric acid, using methyl orange as an indicator. The aniline and pyridine were freshly redistilled and made up accurately by weight.

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[2] By the courtesy of Mr. B. W. Nordlander of the Research Laboratory of the General Electric Company. The special apparatus employed in this determination is described in an internal report of the Research Laboratory.

[3] The writers wish to thank the Philadelphia Quartz Company for their courtesy in supplying not only the silicate used in this research but also information concerning analysis, composition of the silicate, and other valuable data.

TABLE 1

The effect of weak bases on the time of set and the pH of mixtures of sodium silicate and acetic acid at 25°C.

Concentrations constant throughout are as follows: NaOH, 0.395; SiO_2, 0.664; CH_3COOH, 0.454

CONCENTRATION OF BASE	TIME OF SET	pH	CONCENTRATION OF BASE	TIME OF SET	pH
Effect of ammonium hydroxide, NH_4OH			Effect of methylamine, $CH_3NH_2 \cdot HOH$		
gram-moles per liter	*minutes*		*gram-moles per liter*	*minutes*	
0	22.60	5.52	0	22.75	5.52
0.00422	20.50		0.00422	20.25	
0.0105	18.00		0.0105	17.75	
0.0169	15.75		0.0169	15.00	
0.0211	14.00	5.63	0.0211	13.50	5.67
0.0316	10.25		0.0316	9.75	
0.0422	7.25	5.97	0.0422	6.50	5.97
Effect of dimethylamine, $(CH_3)_2NH \cdot HOH$			Effect of trimethylamine, $(CH_3)_3N \cdot HOH$		
0	22.50	5.52	0	22.75	5.52
0.00422	19.80		0.00422	19.30	
0.0105	17.00		0.0105	16.00	
0.0169	14.50		0.0170	12.75	
0.0211	12.50	5.67	0.0211	11.00	5.67
0.0316	9.00		0.0316	7.50	
0.0422	5.60	6.00	0.0422	4.50	5.99
Effect of pyridine, C_5H_5N			Effect of aniline, $C_6H_5NH_2$		
0	22.75	5.52	0	23.00	
0.00422	20.75		0.00422	22.75	
0.0105	18.75		0.0105	22.50	
0.0170	16.75		0.0170	22.00	
0.0211	15.75	5.63	0.0211	21.50	
0.0316	12.50		0.0316	21.00	
0.0422	10.50	5.87	0.0422	20.50	

The results obtained on the time of set of the mixtures of sodium silicate and acetic acid with varying amounts of ammonium hydroxide or the various amines are given in table 1. The values for the pH of the mixtures as determined by the quinhydrone method are also tabulated.

The results shown in table 1 are plotted in figure 1. The effect of the six weak bases is shown graphically, the decrease in the time of set being greatest for trimethylamine and least for aniline. From the four curves for the trimethylamine, dimethylamine, methylamine, and ammonia, together with the pH data, there is a small, though easily evident, specific effect here. The effect of the trimethylamine is evidently the greatest.

We have not found aqueous solutions of pyridine to show an effect as noticeable as that reported by Prasad and Hattiangadi. We were unable to make pH determinations by means of the quinhydrone electrode in the case of the addition of aniline, because the aniline and the quinhydrone apparently react chemically.

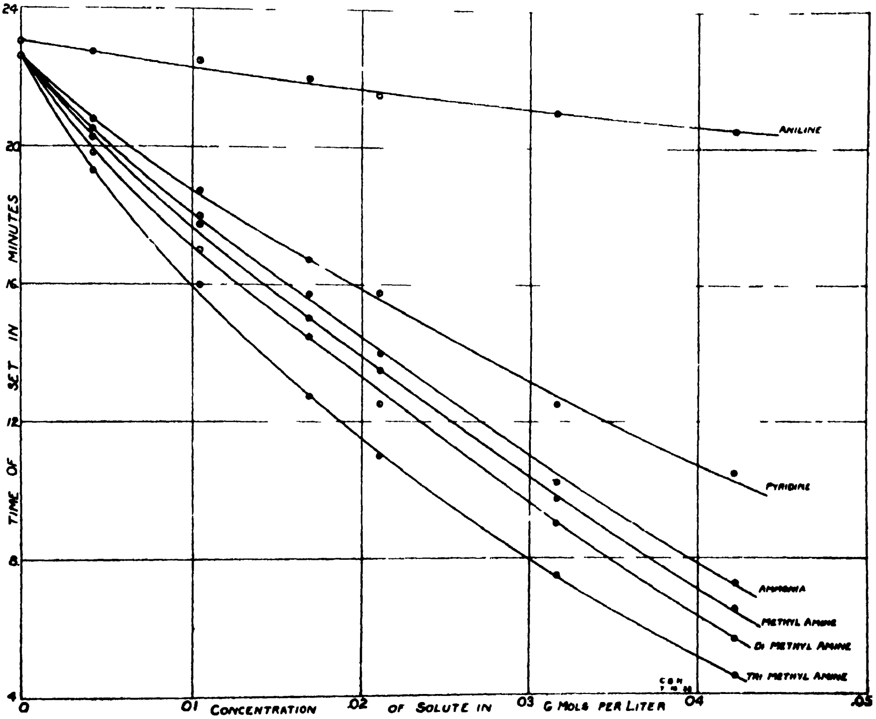

FIG. 1. EFFECT OF VARIOUS WEAK BASES UPON THE TIME OF SET

We have also attempted to analyze the effect of a typical ester, ethyl acetate, which was found to retard the setting of a silicic acid gel. Four series of determinations of the time of set were made, all at 22°C., and all using the same amounts of sodium silicate and acetic acid. The first series, table 2 (1), contained increasing amounts of ethyl acetate; the second contained extra amounts of acetic acid equivalent in concentration to the ethyl acetate of table 2 (1); the third series contained amounts of alcohol equivalent to the ethyl acetate of table 2 (1); and the fourth contained amounts of alcohol and extra acetic acid each equivalent to the ethyl acetate of table 2 (1), in other words, the products of the complete hydrolsis of the ethyl acetate of table 2 (1).

The results in table 2 show the effect of the addition of ethyl acetate and the products of its hydrolysis separately and together. The effect of the ethyl alcohol is obviously practically negligible at these concentrations.

TABLE 2

The effect of ethyl acetate and the products of the hydrolysis of ethyl acetate at 22°C.

Concentrations constant throughout are as follows NaOH, 0 395; SiO_2, 0 664; CH_3COOH, 0 454

CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET
(1) Effect of ethyl acetate		(2) Effect of extra acetic acid	
gram-moles per liter	*minutes*	*gram-moles per liter*	*minutes*
0	28 50	0	29 50
0 0166	30 00	0 0166	38 00
0 0416	36 50	0 0416	51 00
0 0830	44 00	0 0830	69 00
0 125	52 25	0 125	89 00
0 166	60 00	0 168	110 00
(3) Effect of ethyl alcohol		(4) Effect of the products of hydrolysis of ethyl acetate	
0	30 50	0*	29 50
0 0166	30 50	0 0166	37 50
0 0416	31 50	0 0416	51 75
0 0830	31 00	0 0830	69 00
0 1250	31 00	0 1250	89 00
0 1665	31 00	0 1665	109 00

* Both ethyl alcohol and extra acetic acid are added and the concentration of each is as given in this column.

The extra acetic acid has the effect of greatly increasing the time whether alone or in the presence of its equivalent of alcohol. The ethyl acetate, therefore, apparently supplies extra acid, being hydrolyzed in the acid environment, the extra acid increasing the time of set.

We have an example here, therefore, of a type of compound which causes a change in the time of set because it supplies more acid to the gel mixture. Whether the ethyl acetate as such gives a specific effect is impossible to say.

In the next portion of the work, a study was made of the effect of a series of typical organic compounds upon the time of set. An aliphatic alcohol, an aldehyde, a ketone, a hydrocarbon, a sugar, and glycerine were investigated. These substances were added to the acetic acid before mixing with the sodium silicate. Table 3 shows the effects of these substances. It will be noted that the hydrocarbon, benzene, is present in very small amount, because of its slight solubility in water. It will also be noted that the alcohol concentrations here are much higher than those involved in the study of the effect of ethyl acetate.

TABLE 3

Effect of various organic compounds on the time of set and on the pH at 25°C.

Concentrations constant throughout are as follows: NaOH, 0 395; SiO_2, 0.664; CH_3COOH, 0.454.

CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	pH	CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	pH
Effect of ethyl alcohol			Effect of acetaldehyde		
gram-moles per liter	*minutes*		*gram-moles per liter*	*minutes*	
0	20 50	5 52	0	20 5	5 55
0 1910	21 25		1 02	24 0	
0 955	25 00		2 04	28 5	5 55
1 910	28 75	5 52	3 06	32 0	
2 865	33 25		4 08	36 0	5 55
3 810	37 00	5 52			
Effect of acetone			Effect of benzene		
0	21 25	5 52	0	22 00	
0 1515	24 25		0 00001	22 25	
0 7575	27 75		0 00005	22 00	
1 515	31 50	5 52	0 00010	22 00	
2 278	36 50		0 00015	22 25	
3 030	42 50	5 52	0 00020	22 00	
Effect of cane sugar			Effect of glycerine		
0	21 00	5 55	0	21 00	5 55
0 065	21 25		0 152	21 25	
0 130	21 25	5 55	0 760	21 75	
0 195	21 50		1 520	22 00	5 55
0 260	21 25	5 55	2 280	22 25	
			3 040	22 50	5 55

The results of these six sets of data in table 3 are shown graphically in figure 2.

An analysis of the effects of ethyl alcohol, acetaldehyde, acetone, benzene, cane sugar, and glycerine may be attempted as follows. The benzene may only be added in such minute quantities that it is not surprising that we have found no apparent effect. It may be concluded, however, that benzene, if it possesses any specific effect on the time of set, does not possess a large one. The cane sugar shows an effect which is practically negligible. Glycerine shows a slight effect. It should be noted that the maximum concentration of cane sugar obtained was 0.26 molar, while the glycerine reached 3.04 molar. The effect on the pH by these compounds was also shown to be very slight. The effects of ethyl alcohol, acetaldehyde, and acetone upon the pH of these sodium silicate–acetic acid mixtures when added up to concentrations of 3 to 4 molar are seen to be negligible when measured by the quinhydrone method. The effects on the time of set, however, are perfectly evident. Each one lengthens the time of set, and the effect of the acetone is greater than the effects of the other two. The effects of these compounds are apparently specific, since no change of pH could be detected.

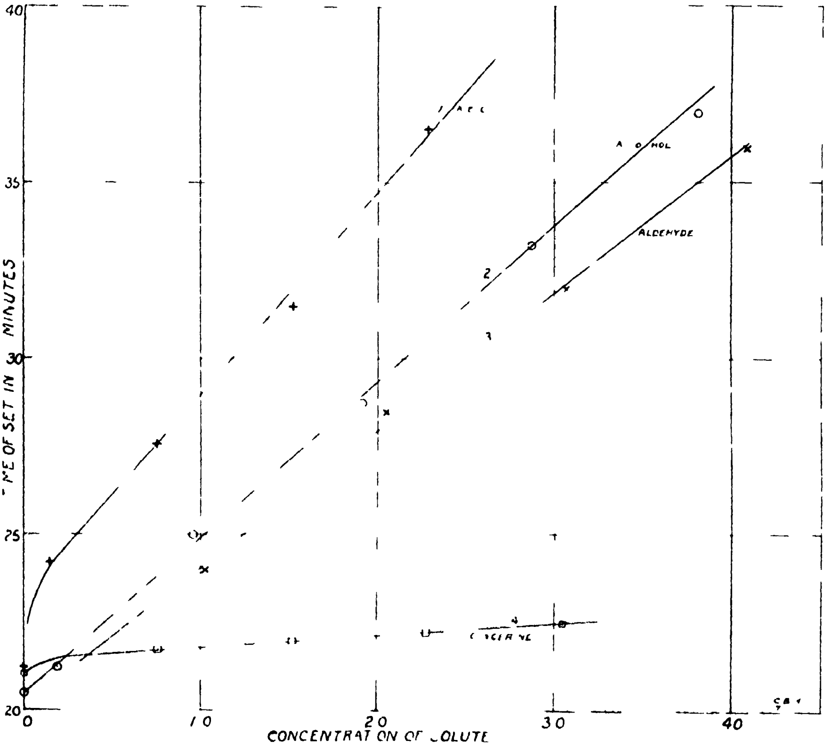

FIG. 2. EFFECT OF SOLUTES UPON THE TIME OF SET

It will perhaps be possible in the future to correlate these results with the results of other investigators on other properties of these gel mixtures.

SUMMARY

The effects of added solutes on the time of set of gel mixtures produced by mixing solutions of acetic acid and sodium silicate have been studied. An attempt has been made to separate the specific effects of the compounds themselves from the effects which they produce by changing the pH of the mixtures.

Ammonium hydroxide, methyl-, dimethyl-, and trimethyl-amines, pyridine, and aniline up to 0.04 *M* decrease the time of set mainly by increasing the pH of the mixture. There is, however, a specific effect apparent, greatest in the case of trimethylamine.

A typical ester, ethyl acetate, apparently increases the time of set chiefly because of acetic acid set free during acid hydrolysis of the ester.

Cane sugar and glycerine have little effect either on the time of set or on the pH. Benzene shows no effect, although its very low solubility practically precludes any save a very unusual effect.

Ethyl alcohol, acetaldehyde, and acetone show practically no effect upon the pH, but show considerable specific effects in increasing the time of set.

REFERENCES

(1) Hurd and Letteron: J. Phys. Chem. **36**, 604 (1932).
(2) Werner: J. Am. Pharm. Assoc. **9**, 501 (1920).
(3) Kröger: Kolloid-Z. **30**, 16 (1922).
(4) Bhatnagar and Mathur: Kolloid-Z. **30**, 368 (1922).
(5) Prasad and Hattiangadi: J. Indian Chem. Soc. **6**, 653, 893, 991 (1929).
(6) Holmes: J. Phys. Chem. **22**, 510 (1918).
(7) Prasad and Hattiangadi: J. Indian Chem. Soc. **6**, 893 (1929).
(8) Maschke: Ann. Physik. **222**, 90 (1872).
(9) Pappada: Gazz. chim. ital. **33**, 272 (1903); **35**, i, 78 (1905).
(10) Wulf and Praetorius: Rec. trav. chim. **49**, 582 (1930).

THE SOLUBILITY OF OXYGEN IN GOLD AND IN CERTAIN SILVER-GOLD ALLOYS

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INTRODUCTION

In earlier papers on the subject of the solubility of gases in metals, one of us (F. M. G. J.) (1), in collaboration with E. W. R. Steacie, has discussed the solubility of oxygen and of hydrogen in silver. The present paper is concerned with the solubility of oxygen in gold and in certain gold-silver alloys.

Little is known of the solubility of oxygen in gold. The early work of Graham (2) indicated an absorption of 0.006 volume of oxygen per volume of metal. Later workers (3) obtained contradictory results, which may be partly explainable by surface effects. Bone and his coworkers (4) obtained some evidence of the occlusion of oxygen by gold wire, but the experimental conditions were such that the conclusion that appreciable amounts of oxygen are absorbed appears somewhat doubtful.

The solubility of oxygen in alloys of the noble metals has received small attention. Some observations of a qualitative nature are to be found in the early literature. Sieverts and Krumbhaar (3) studied quantitatively the solubility of oxygen in alloys of gold and silver, in the molten state, at 1123°C. So far as is known to us, no quantitative work on the solubility of this gas in solid silver-gold alloys has been published.

APPARATUS

The experimental method was the same in principle as that described in detail in previous communications. A known volume of gas is introduced into a calibrated silica bulb of about 10 cc. capacity, which contains the metal foil under investigation and which is connected to a mercury manometer. At any temperature the pressure of the gas in the bulb can be calculated by the gas laws. If any absorption takes place, the observed pressure will be less than the calculated value and the difference between the two pressures will be a measure of the amount of gas which has been dissolved by the metal.

At the conclusion of an experimental run, the gas is pumped out of the bulb and measured. This procedure affords a check on the apparatus and eliminates errors due to incomplete evacuation of the metal. All experiments in which the volume of recovered gas differed from that originally admitted to the bulb were discarded.

Temperatures were measured by a constant-volume nitrogen thermometer consisting of a silica bulb of approximately the same size as that containing the metal under observation. The two bulbs were placed side by side in the furnace, any temperature variations in different regions being thus automatically compensated.

When a fresh sample of metal was placed in the bulb the temperature was raised to 850–900°C. and kept there for six hours while the bulb was evacuated by means of a condensation pump backed by a Toepler pump. Thereafter during the succeeding experiments, extending in most cases over months, the temperature varied between that of the room and 850–900°C. Any crystal strain caused by the cold-rolling of the metal into foil must have been destroyed by this treatment.

With the exception of some minor changes the apparatus was identical with that already described (1a).

MATERIALS

Commercially pure gold was further purified by the method of Krüss (5). The metal was then fused under borax in a silica tube, cleaned by scrubbing with sand, and rolled into sheets about 0.15 mm. thick. Two samples of gold were employed, having volumes of 1.32 and 2.89 $cm.^3$ respectively.

The silver used for the preparation of the alloys was purified by a method due to Stas (6) and prepared in the same form as the gold.

The alloys were prepared by weighing out the calculated quantities of purified gold and silver and fusing the mixture in a silica tube. When fused, the metal was thoroughly stirred with a silica rod, allowed to solidify, cooled, cleaned with sand, and rolled into sheets. Alloys of 5, 10 and 20 per cent of gold were employed, the volume of metal being 2.65, 2.76, and 3.60 $cm.^3$ respectively. One sample of each alloy was investigated.

Nitrogen and oxygen, obtained from cylinders of the compressed gas, were purified by the usual methods and stored over phosphorus pentoxide.

EXPERIMENTAL RESULTS

At the conclusion of the experiments the various metals showed, on examination, little evidence of change. No surface changes could be observed in the *gold* (second sample), although it had lost 0.03 gram in weight. The edges of the foil had sintered together and the probability is that the small loss in weight is due to evaporation. The silver–gold alloys had developed a crystalline surface and the evaporated silver from the alloy containing 5 per cent of gold had imparted a slight brownish tinge to the silica. A small loss in weight occurred, with partial sintering of the edges of the foil.

Solubility of nitrogen

No measurable absorption of nitrogen either by gold or by the three alloys of gold and silver, over the temperature range 200–900°C., was found.

Solubility of oxygen

A. In gold. Preliminary experiments using a Pyrex bulb indicated a small solubility, of the order of 0.01 volume at 500°C. and under a pressure of 60 cm. of mercury. The solubility decreased with decreasing temperature and pressure, but the magnitude of the absorption was too close to the experimental error of the apparatus to allow of satisfactory measurement. It appeared possible that at higher temperatures and pressures the effect might become measurable, and accordingly further experiments were carried out, using a silica bulb. In this second series of twelve experiments, the pressure varied from 10 to 70 cm. of mercury and the temperature from 300°C. to 900°C. The solubility as measured by these experiments was small, in no case exceeding 0.014 volume, but varied irregularly with temperature and pressure, owing, in part, to the high percentage error of the apparatus. The results are given in table 1.

TABLE 1

Solubility of oxygen in gold (sample 2) in a silica apparatus

TEMPERATURE	PRESSURE	ABSORPTION	TEMPERATURE	PRESSURE	ABSORPTION
degrees C	*cm* Hg	*volumes per volume*	*degrees C*	*cm* Hg	*volumes per volume*
900	14 0	0 002	750	63 9	0 007
	19 4	0 000		68 4	0 005
	30 7	0 005	700	28 1	0 006
850	13 9	0 002		33 3	0 010
	30 1	0 005		58 5	0 003
	66 7	0 010		61 2	0 007
800	29 5	0 005	600	55 3	0 002
	35 1	0 010		57 9	0 006
	61 0	0 005		63 2	0 007
	64 5	0 004	550	11 9	0 009
	65 3	0 008		25 9	0 014
	70 0	0 003	500	51 0	0 003
750	18 2	0 002		55 4	0 007
	28 8	0 005	400	27 7	0 011
	34 2	0 002		50 5	0 002
	59 5	0 005	320	45 2	0 001

These figures indicate that oxygen is absorbed by gold to a small extent,

TABLE 2

Values of k at different values of P and Q

Alloy No. 3: 20 per cent gold, 80 per cent silver

Temperature 900°C log *a* = 1.135

P	Q	k (CALCULATED)
10 7	0 043	0 486
14 9	0 050	0 486
24 9	0 063	0 478
54 3	0 090	0 473
63 2	0 099	0 478
93 6	0 117	0 474

TABLE 3

Solubility (volumes per volume of metal) of oxygen in silver–gold alloys

Alloy No. 1: 5 per cent gold, 95 per cent silver

PRESSURE	T = 200	300	400	500	600	650	700	750	800	860°C
	k = 0 328	0 286	0 183	0 309	0 334	0 397	0 548	0 554	0 543	0 533
cm										
10	0 039	0 040	0 043	0 043	0 048	0 049	0 043	0 047	0 060	0 076
20	0 049	0 049	0 049	0 053	0 061	0 065	0 062	0 072	0 088	0 110
30	0 055	0 055	0 053	0 060	0 070	0 076	0 078	0 089	0 109	0 138
40	0 061	0 060	0 056	0 066	0 078	0 085	0 090	0 105	0 127	0 160
50	0 065	0 064	0 059	0 071	0 083	0 093	0 102	0 119	0 144	0 180
60	0 069	0 067	0 061	0 074	0 088	0 100	0 113	0 132	0 150	0 198
70	0 073	0 070	0 063	0 078	0 092	0 107	0 123	0 144	0 172	0 215
80	0 076	0 073	0 065	0 081	0 096	0 112	0 132	0 154	0 185	0 236

TABLE 4

Solubility (volume per volume of metal) of oxygen in silver–gold alloys

Alloy No 2 10 per cent gold, 90 per cent silver

PRESSURE	T = 200	300	400	500	600	650	700	750	800	860°C
	k = 0 045	0 037	0 042	0 178	0 280	0 462	0 583	0 573	0 536	0 545
cm										
5	0 044	0 043	0 039	0 033	0 029	0 022	0 018	0 022	0 029	0 039
10	0 045	0 043	0 040	0 037	0 036	0 031	0 027	0 033	0 042	0 056
20	0 046	0 044	0 042	0 042	0 043	0 043	0 040	0 049	0 061	0 083
30	0 046	0 044	0 042	0 045	0 048	0 052	0 050	0 062	0 076	0 103
40	0 047	0 045	0 044	0 047	0 052	0 059	0 059	0 072	0 088	0 120
50	0 048	0 045	0 045	0 049	0 055	0 065	0 068	0 082	0 100	0 136
60	0 049	0 046	0 046	0 050	0 058	0 071	0 075	0 091	0 110	0 150
70	0 049	0 046	0 047	0 052	0 061	0 077	0 082	0 100	0 119	0 164
80	0 049	0 046	0 047	0 053	0 063	0 082	0 089	0 107	0 128	0 176

which probably does not exceed one-hundredth of a volume at 900°C. and under atmospheric pressure, and is consequently not much larger than the experimental error of the method (0.002 volume). The results obtained are not wholly consistent with each other, and although many experiments were made in an endeavor to obtain greater precision, it was found impossible to reproduce results at a given temperature within the known experimental error. The difficulty cannot be wholly ascribed to the large percentage error of the measurements; there appears to be some other factor entering into the solubility relationship. Whether, however, this is a surface phenomenon, or hysteresis due to the thermal history of the metal or to some other obscure cause, cannot be elucidated without further investigation.

TABLE 5

Solubility (volume per volume of metal) of oxygen in silver-gold alloys

Alloy No. 3: 20 per cent gold, 80 per cent silver

PRESSURE	T = 200	300	400	500	600	650	700	750	800	850	900°C
	k = 0 121	0 124	0 094	0 084	0 155	0 236	0 415	0 395	0 498	0 474	0 480
cm.											
10	0 053	0 049	0 049	0 050	0 047	0 041	0 028	0 025	0 026	0 034	0 041
20	0 058	0 053	0 052	0 053	0 052	0 047	0 037	0 033	0 037	0 047	0 057
30	0 061	0 056	0 055	0 055	0 056	0 053	0 044	0 039	0 045	0 057	0 070
40	0 063	0 058	0 056	0 056	0 059	0 057	0 050	0 043	0 051	0 065	0.080
50	0 065	0 060	0 057	0 057	0 061	0 060	0 055	0 047	0 057	0 072	0 089
60	0 066	0 061	0 058	0 058	0 062	0 063	0 059	0 051	0 062	0 079	0 097
70	0 061	0 062	0 059	0 058	0 064	0 065	0 063	0 054	0 067	0 085	0 106
80	0 069	0 064	0 060	0 059	0 066	0 067	0 067	0 057	0 071	0 090	0 113

The results show, however, that there is a small absorption of oxygen by gold, although nothing can be deduced as to the variation of the solubility with temperature and pressure The comparative insolubility of oxygen in gold established by these measurements is in agreement with the results of Sieverts and Krumbhaar (3).

B. In silver–gold alloys. The solubility of oxygen in silver has been shown to be proportional, at any fixed temperature, to the square root of the pressure, and this relationship can be represented by the equation

where Q is the solubility, expressed as volumes of gas per volume of metal, P is the pressure, and the coefficient a depends on the temperature.

The solubility of oxygen in silver–gold alloys has been found to conform to this equation only at higher temperatures, but the expression

$$Q = aP^k$$

adequately expresses the results over the whole temperature range investigated. In this equation, the exponent k is equal to $\frac{1}{2}$ at all temperatures above a certain "critical" temperature (700–750°C.), which appears to be independent of the composition of the alloy. Below this temperature, k decreases with decreasing temperature. The experimental results were obtained by fixing the temperature at the desired point and measuring the solubility under pressures of oxygen varying from 5 to 80 cm. of mercury. If the logarithm of the solubility is then plotted against the logarithm of the pressure, the slope of the resultant straight line gives the value of k for that temperature, while the intercept on the y-axis is a measure of log a. By inserting these values in the equation, the solubility at pressures of 5, 10, 20, etc., cm. can be calculated.

Tables 3, 4, and 5 give the values of the solubility of oxygen in the three alloys investigated. To illustrate the constancy of k, table 2, in which P is the actual pressure of the gas and Q the corresponding solubility, is inserted.

DISCUSSION OF RESULTS

Solubility of oxygen in silver–gold alloys

The variation of the solubility with the pressure of oxygen is illustrated in figures 1 and 2, taken from the results obtained with an alloy containing 10 per cent of gold. At temperatures above 700°C., the solubility is approximately proportional to the square root of the pressure ($k = \frac{1}{2}$), while below this temperature the exponent k decreases, although the curve remains a straight line. This statement applies to all three alloys investigated, with the reservation that in the case of the alloy richest in gold (20 per cent) the "critical" temperature is higher, viz., at 750°C.

The variation of solubility with temperature is shown in figures 3, 4, and 5. In figure 3 is included, for purposes of comparison, the curve of solubility of oxygen in pure silver under a pressure of 80 cm. of mercury. It will be seen that the solubility curves of oxygen in this alloy show a general resemblance to those of the system oxygen–silver, but only at the higher pressures and for temperatures above 400°C. Below this temperature the solubility does not increase so markedly as in the latter system. Inspection of the curves for the pressures 40, 30, 20, and 10 cm. reveals the gradual appearance of a minimum at 700°C. in the solubility curve, which at 40 cm. is a mere inflection in the curve, but at 10 cm. is strongly marked. It will also be noticed that the minimum found to exist in the solubility of oxygen in silver is indicated, in the case of this alloy, at the higher pressures, but disappears as the pressure of the gas diminishes.

The curves of solubility versus temperature for the second alloy (90

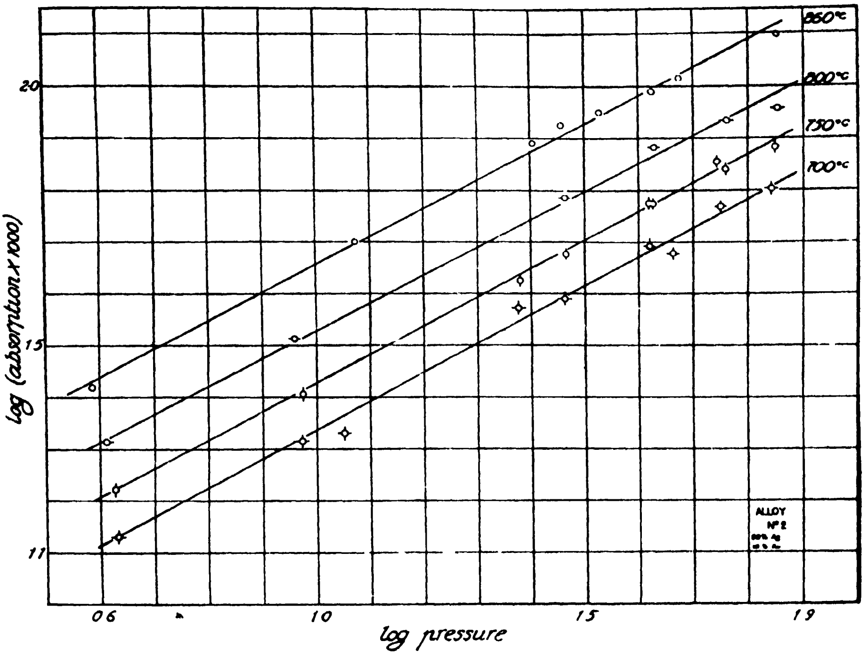

FIG. 1. VARIATION OF SOLUBILITY WITH PRESSURE AT TEMPERATURES ABOVE 700°C. Silver 90 per cent; gold 10 per cent

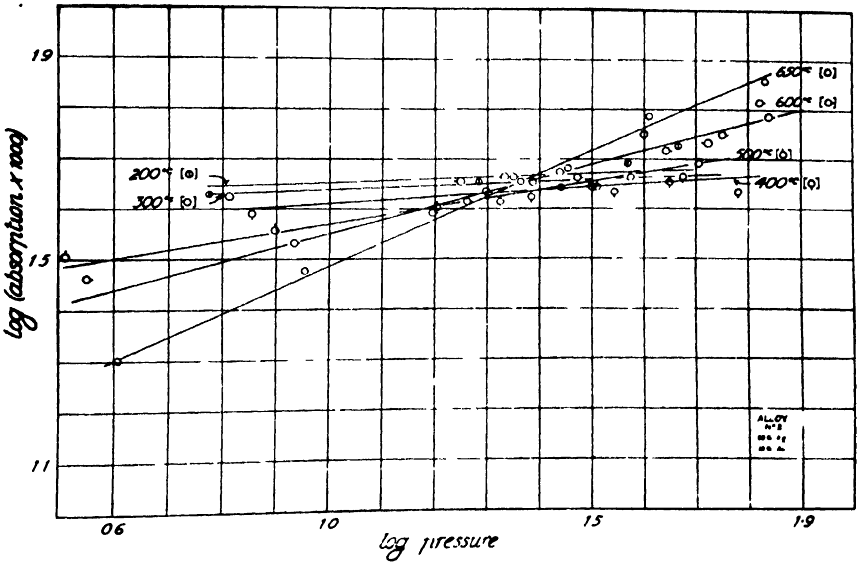

FIG. 2. VARIATION OF SOLUBILITY WITH PRESSURE AT TEMPERATURES BELOW 700°C. Silver 90 per cent; gold 10 per cent

per cent Ag, 10 per cent Au; figure 4) exhibit a minimum at 700°C. in a more strongly marked form, and here it does not disappear at the higher pressures. The drawing-together of the curves at low temperatures is also more pronounced than in the alloy richer in silver, and there is no indication of the minimum at 400°C., even at a pressure of 80 cm. With the

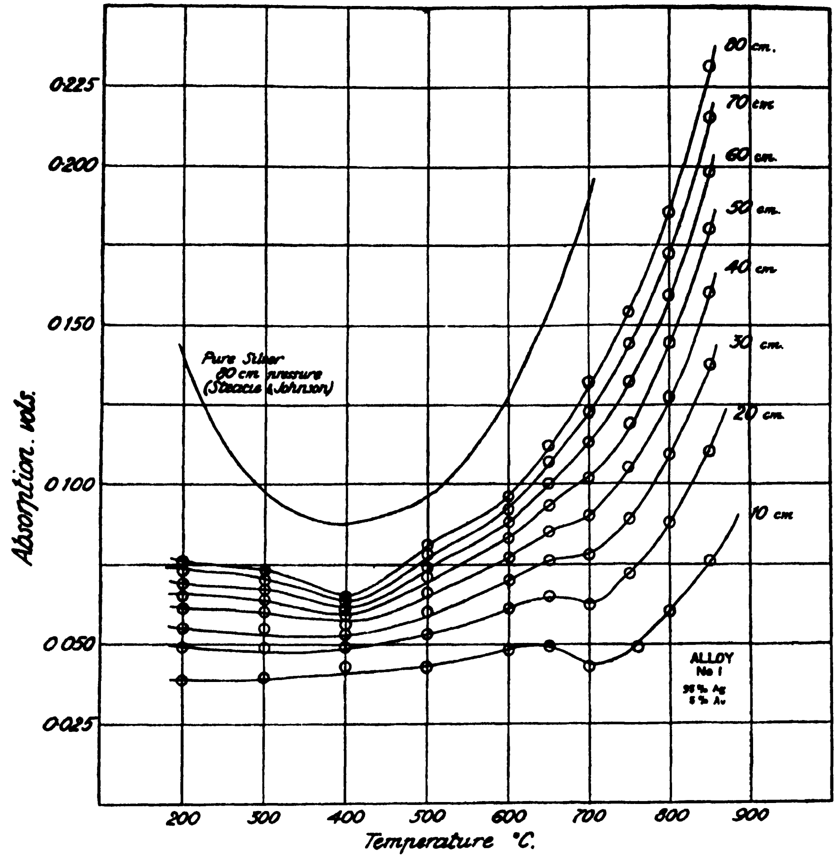

FIG. 3. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 95 per cent; gold 5 per cent

TABLE 6

ALLOY NUMBER	COMPOSITION	A	MELTING POINT
		degrees C	*degrees C.*
1	95 per cent silver: 5 per cent gold	1040	970
2	90 per cent silver: 10 per cent gold	980	980
3	80 per cent silver: 20 per cent gold	1025	1010

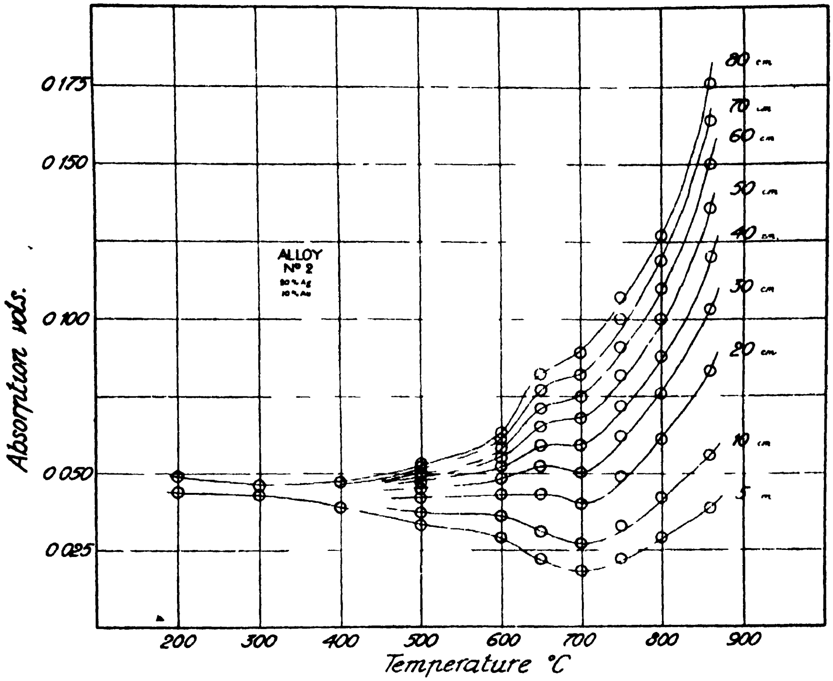

FIG. 4. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 90 per cent; gold 10 per cent

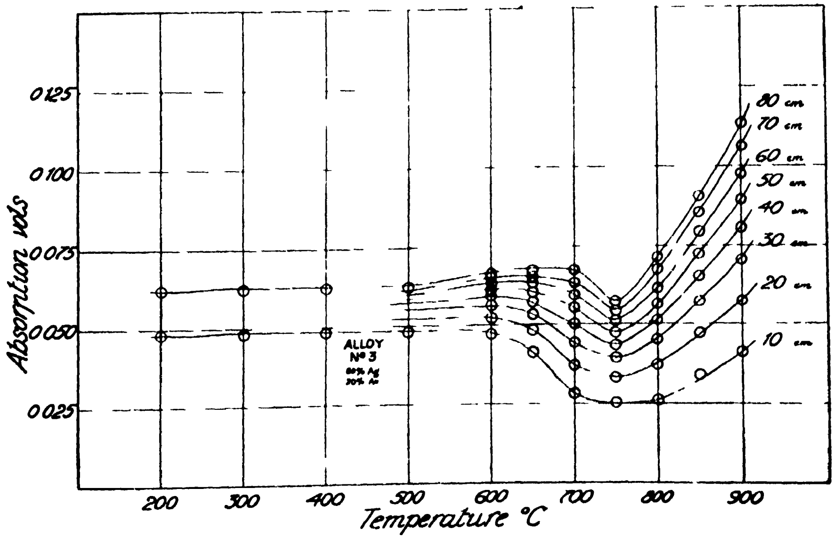

FIG. 5. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 80 per cent; gold 20 per cent

third alloy (80 per cent Ag, 20 per cent Au; figure 5), the 400°C. minimum is also completely absent. The inflection in the curves at the higher temperature, however, has developed still more strongly. The curves below 500°C. are here represented as parallel to the temperature axis, which means that for the temperatures 500–200°C. the solubility results for each pressure are the same for all these temperatures within the experimental error.

As mentioned before, the difficulties of establishing the log absorption versus log pressure curve for temperatures below 400°C. have made these results less reliable than those at higher temperatures; for this reason only the extreme pressure values are drawn in the curves representing the variation of solubility with temperature, the other values lying within these limits. At these temperatures, the most that can be said is that with the two alloys richer in gold (alloy No. 2, alloy No. 3), the solubility appears to approach a value of about 0.05 volume, which is the same for both alloys. With the alloy richest in silver there is some indication that for higher pressures of oxygen an increase in the solubility value takes place from 400°C. to 200°C., a behavior which is similar to that of pure silver (figure 3). The effect, however, is very much less, even in this case, than was found with silver.

The relationship between solubility and temperature for the three alloys of silver and gold examined is thus a complicated one. Above the temperature at which the minimum occurs, the curves for all pressures, in the range investigated, are parallel for each alloy. Below this temperature complications are added, and it is hence not possible to express the results for all temperatures by a concise equation. For temperatures above the "critical" temperature, the equation

$$\frac{1}{Q} = K_1 (A - t)$$

has been found to hold. Here, Q is the solubility, t the temperature in degrees Centigrade, K_1 a coefficient specific for each pressure and each alloy, and A varies between 980°C. and 1040°C. as shown in table 6. The value of A thus approximates to the melting point of the alloy. This is in agreement with results for the system oxygen-silver (1).

The variation of solubility with concentration of gold in the alloy is shown for the temperature 800°C. in figure 6, in which the values for the solubility of oxygen in pure silver are taken from Steacie and Johnson's results. The change of solubility with concentration for the eight pressures 10 to 80 cm. forms a family of smooth curves which, for this temperature, can be expressed by the equation

$$\frac{1}{Q} = K_2 (C + 5\,7)$$

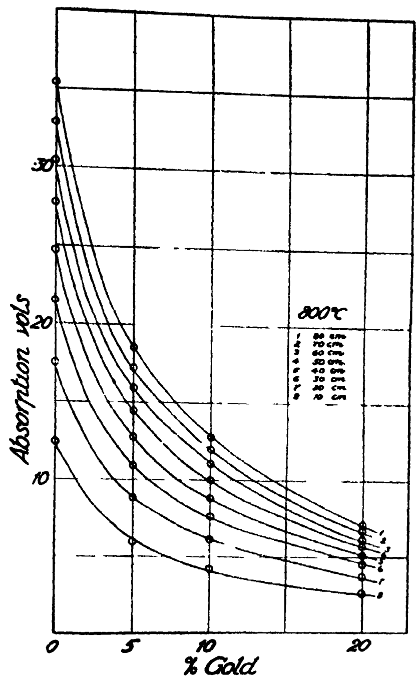

FIG. 6. VARIATION OF SOLUBILITY WITH CONCENTRATION AT 800°C.

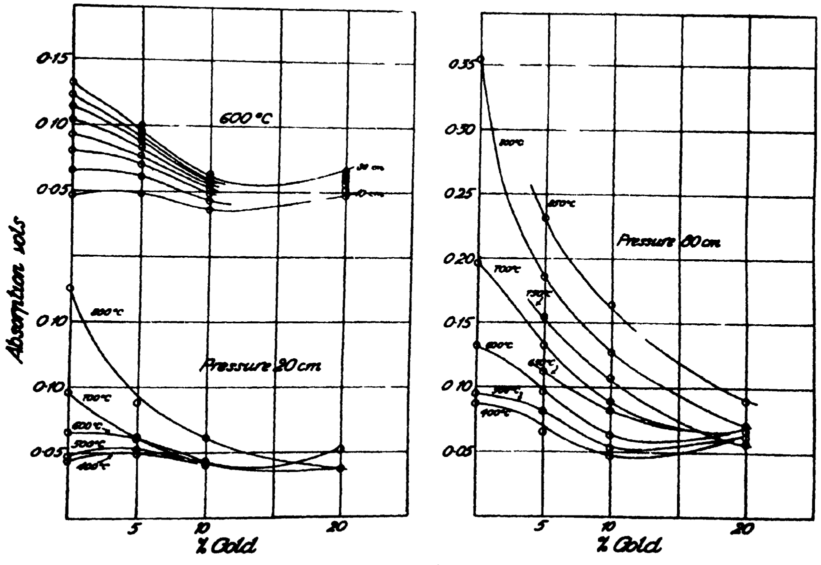

FIG. 7. VARIATION OF SOLUBILITY WITH CONCENTRATION AT VARIOUS TEMPERATURES AND PRESSURES

where C is the concentration (per cent) of gold, and the coefficient K_2 varies with the pressure.

Similar curves for other temperatures and pressures are given in figure 7.

GENERAL DISCUSSION

Solubility of oxygen in silver–gold alloys

The experimental results have been summarized in the foregoing section, and the effect of various factors on the solubility has been discussed. Above a certain "critical" temperature, which apparently varies with the concentration of gold, the factors affecting the solubility of oxygen in the three alloys examined appear to be the same as those previously found to condition the solubility of the gas in pure silver, i.e., the solubility is proportional to the square root of the pressure. As the temperature is reduced below the critical temperature, however, this relationship no longer holds; the exponent k in the equation

$$Q = aP^k$$

becomes less than $\frac{1}{2}$ and decreases with decreasing temperature to an extent varying with the composition of the alloy.

The behavior of the solubility-pressure relationship is reflected in the solubility-temperature curves, and is partly responsible for the inflection in the curves at the so-called critical temperature. This dip is most marked at low pressures and becomes more strongly defined with increasing concentration of gold. The curves representing the solubility-temperature relationship for the solubility of oxygen in silver exhibit a minimum at 400°C.; below this temperature and above it, the solubility increases, but remains for all temperatures related to the pressure by the expression $Q = aP^{\frac{1}{2}}$; no trace of any variation in the exponent of P with temperature was found. It appears to be established, therefore, that the form of the curves connecting solubility and temperature for these three alloys is due to the presence of gold.

The measurements of the solubility of oxygen in pure gold show that a small absorption of the gas occurs, which appears to decrease with decreasing temperature and pressure. Any admixture of this practically inert metal with silver would therefore be expected to diminish the solubility of oxygen according to some simple function of the concentration of gold. That it actually does so at high temperatures is shown by the equation

$$\frac{1}{Q} = K_2\,(C + 5.7)$$

which applies only at temperatures above those at which irregularity appears in the solubility-temperature curves for the different alloys.

It has been suggested that the minimum in the solubility-temperature curves for oxygen and silver might perhaps be due to the change from one allotropic form of silver to another, or to a change in the manner of combination with oxygen. In a similar way, it could be argued that the form of the solubility-temperature curves for oxygen in these alloys is caused by the formation of some compound of gold and silver which is stable only at temperatures below 750°C. To this suggestion, however, there is the objection that all the measured properties of gold silver alloys show a gradual change as the concentration changes, and give no indication of any interruption in the curve, such as would be caused by the existence of a compound. Thus Holgersson (7) in an x-ray study of gold–silver alloys by the Debye-Scherrer method, found that the length of side of the unit cube is very nearly a linear function of the atomic composition. Measurements of the physical properties of the alloys, such as specific heat, electrical conductivity, etc., all support the conclusion from freezing point data that these two metals form no compound.

The view that the existence of this "critical" temperature is due to change in the crystal state of the metal is not accepted. Any strains in the crystal lattice caused by cold-working of the metal would be eliminated by the heat treatment incidental to the experiments; and the completely reproducible results below this critical temperature show that gradual recrystallization can have little effect on the solubility of oxygen in these alloys.

The effect of surface

It is possible that the irregularities in the solubility-temperature curves are due to surface effects.

If it be assumed that the true solubility falls off uniformly with the temperature, in the manner indicated by the solubility of oxygen in silver, that is, with a minimum at 400°C., below which the solubility increases, and if it be further assumed that, as the temperature is decreased below 750–700°C., surface effects begin to appear, rapidly increasing below 700°C. until 500°C. or so is reached, then an apparent solubility curve of the form actually obtained would result. This is shown diagrammatically in figure 8.

Lack of time has prevented the investigation of more than one sample of each alloy. Certain deductions can, however, be made from the results obtained. The metal was used in the form of foil, rolled to a thickness of 0.1 mm. The surface can therefore be calculated from the mass of metal, its density, and the thickness of the foil, but many factors affect the calculation. (1) The thickness of the foil varies in different places. (2) The foil, after being used for a time, develops a crystalline appearance, which indicates a largely increased surface. (3) Distillation of the metal takes place to some extent to the walls of the silica bulb.

The surface of the metal as calculated from the volume and the thickness is affected by these uncertainties to an extent which is quite unknown, and which might easily vitiate any attempted control of the surface area. If, however, these uncertain factors are neglected, a numerical calculation will show that the surface of the metal may account for a considerable apparent solubility of oxygen in the alloy. In the experiments on alloy No. 3, the volume of metal was 3.60 cm.^{3}, its thickness 0.01 cm.; hence its calculated surface was 720 cm.^{2} The volume of the bulb and dead space was approximately 10 cm.^{3} If we adopt Langmuir's theory of a unimolecular layer as the maximum amount of gas which the metal can adsorb on its surface and assume that at the lower temperatures the surface is saturated, then the number of molecules adsorbed on the surface can be calculated.

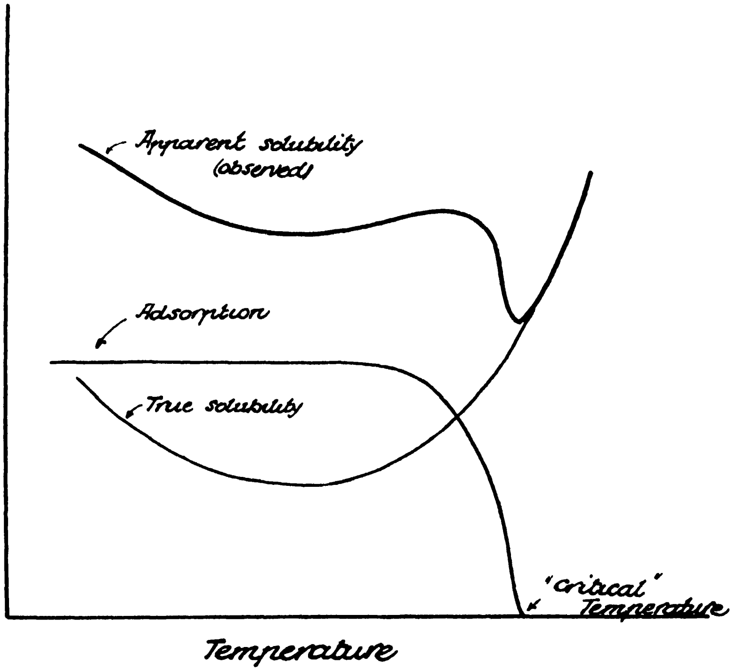

FIG. 8

The radius of the oxygen molecule is 1.5 × 10^{-8}cm.; hence its (projected) area is 7 × 10^{-16} cm.^{2} The number of oxygen molecules adsorbed on a surface of 720 cm.^{2} in a unimolecular layer is, therefore, 10^{18}. By the gas laws, this number of molecules, in a space of 10 cm.^{3} in volume, would exert, at 0°C. a pressure of 0.28 cm. At higher temperatures the pressure would vary according to the law of Charles, and at 200°C. would be approximately 0.5 cm. Hence, at 200°C. the gas molecules adsorbed in a complete unimolecular layer on the surface of the metal would cause a pressure drop of 0.5 cm. This corresponds, using the constants of the apparatus in the case of this particular alloy, to an apparent solubility of 0.01 volume of gas per volume of metal. The apparent solubility as measured is about 0.05 volume, which, taking into account the very approximate nature of the calculated value and the fact that part of this apparent solubility is undoubtedly due to true solution, is of the same order of magnitude. Furthermore, the crystallization of the metal surface, and the distillation of the metal to the walls of the bulb, would have the effect of largely increasing the surface area of the metal, and hence the pressure drop due to the adsorbed molecules.

The form of the true solubility curve below 400°C. would affect the observed curve to an increasing extent as the pressure is increased, while the effect of adsorption would remain constant for the range of temperature where the surface is completely covered with a layer of molecules of oxygen. In the most favorable case, the increased solubility due to increasing pressure might eventually, at higher temperatures, mask the surface effect altogether. This is apparently so in the case of alloy No. 1, where the minimum at 700°C. disappears at higher pressures; while that at 400°C., on the other hand, develops as the pressure is increased.

It may perhaps be mentioned that the assumption of the persistence of surface effects up to the comparatively high temperature of 750°C. is not without corroboration. Langmuir (8) found that tungsten wire adsorbs appreciable amounts of oxygen up to a temperature of 3000°C., while at 1200°C. the surface of the metal is saturated.

SUMMARY

The solubility of oxygen in gold has been measured over a wide range of temperature at various pressures, and has been found to be of the order of 0.010 volume per volume of metal at the highest temperature (900°C.) and pressure (70 cm. of mercury) employed.

The solubility of oxygen in three silver–gold alloys containing 5, 10, and 20 per cent of gold has been measured at temperatures between 850°C. and 200°C., and under pressures of from 5 to 80 cm. Above a certain temperature the solubility is proportional to the square root of the pressure and is related to the temperature by the equation $1/Q = K_1(A - t)$, where Q is the solubility, t the temperature in degrees Centigrade, and A the melting point of the alloy; the solubility is a function of the concentration which, for each temperature, can be expressed by the equation $1/Q = K_2\ (C + 5.7)$, where C is the percentage concentration of gold in the alloy. Below this "critical" temperature the apparent solubility is related to the pressure by the equation $Q = aP^k$, in which k diminishes with decreasing temperature; the relation between solubility and temperature, and that between solubility and concentration of gold, are complicated by the appearance of minima in the curves.

An explanation of the solubility phenomena at temperatures below the so-called "critical" temperature has been advanced which depends on the assumption of surface effects. This effect of surface first becomes apparent, as the temperature is decreased, at the "critical" temperature.

Nitrogen is insoluble in gold and in silver–gold alloys of the composition investigated.

REFERENCES

(1) (a) STEACIE AND JOHNSON: Proc. Roy. Soc. London **A112**, 542 (1926).
(b) STEACIE AND JOHNSON: Proc. Roy. Soc. London **A117**, 662 (1928).
(2) GRAHAM: Phil. Mag. [4] **32**, 503 (1866).
(3) NEUMANN: Monatsh. **13**, 40 (1892).
SIEVERTS AND KRUMBHAAR: Ber. **43**, 893 (1910).
BENTON AND ELGIN: J. Am. Chem. Soc. **49**, 2426 (1927).
(4) BONE AND COWORKERS: Trans. Roy. Soc. London **A206**, 1 (1906); **A109**, 459 (1925).
(5) KRÜSS: Ann. **238**, 30 (1887).
(6) STAS: Mem. acad. Belg. **33**, 1 (1865).
(7) HOLGERSSON: Ann. Physik **79**, 35 (1926).
(8) LANGMUIR: Phys. Rev. **8**, 149 (1916); Chem. Rev. **6**, 473 (1929).

SOLID POLYIODIDES OF THE ALKALI METALS[1]

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INTRODUCTION

In an earlier paper (1) evidence has been presented for the existence of three solid solvated polyiodides of potassium: $KI_3 \cdot H_2O$, $KI_7 \cdot H_2O$, and a compound containing benzene. Each of these compounds contains solvent molecules which are apparently part of the constitution of these polyiodides, for on the removal of combined solvent the polyiodides decompose, e.g., the dehydration of the triiodide by P_2O_5 (2).

$$KI_3 \cdot H_2O \longrightarrow KI + I_2 + H_2O$$

This, and other experiments, beside indicating that the combined solvent is part of the constitution of these polyiodides, show that solid *unsolvated* polyiodides of potassium are unstable, and do not exist at 25°C. and 1 atmosphere pressure.

While the earlier paper was in the press, Bancroft, Scherer and Gould (3), from a survey of the literature and additional experiments, concluded that potassium polyiodides definitely do not exist at 25°C. They failed, however, to consider the possibility of solvation, which is apparently the key to the problem, and their results when interpreted in this light are actually largely in agreement with the existence of *solvated* polyiodides and in complete agreement with ours as to the non-existence of unsolvated polyiodides of potassium.

Some of their most critical experiments may be reinterpreted. That (4) in which potassium triiodide, prepared by Johnson's method, is shown to exist in equilibrium with an aqueous solution of potassium iodide containing 65.19 per cent iodine, is in excellent agreement with our results (5), which show $KI_3 \cdot H_2O$ to exist in equilibrium with aqueous potassium iodide solutions whose iodine content may be varied between 62 and 66 per cent. This experiment indicates that $KI_3 \cdot H_2O$ is a stable phase in this system under these conditions.

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[1] The experimental part of this paper was carried out as part of the requirements for the degree of Doctor of Philosophy at the Royal College of Science, University of London, and completed in July, 1931.

[2] Commonwealth Fellow.

Bancroft and his associates (6) quote some analyses on three different preparations of potassium triiodide, from which mother liquor had been removed by drying between filter papers and which gave a potassium iodide to polyiodide iodine ratio of 1.002 and totalled ($KI + I_2$) 94.78 per cent (which is very close to $KI_3 \cdot H_2O$). After obtaining these results which indicate $KI_3 \cdot H_2O$, they quote two analyses on wet solid which had not been dried between filter papers and which gave a different potassium iodide to iodine ratio than the above. It is then suggested that drying between filter papers is responsible for this difference and that a large error is introduced by following such a procedure for the preparation of samples for analysis and that this error affects all previous analyses which had indicated the existence of solid potassium triiodide. However, their analyses of the undried wet solid only total ($KI + I_2$) 79.3 and 76.2 per cent, or over 20 per cent of water (by difference). Our results (1) show that $KI_3 \cdot H_2O$ does not exist in equilibrium with more than 8 per cent of water at 25°C., so that it appears very probable that the above wet solid was only potassium iodide wet with solution. This indicates that the difference in potassium iodide to iodine ratios, for the dried and undried samples, did not lie in the difference in treatment, but that in the first case $KI_3 \cdot H_2O$ was the solid phase while in the other the solid was only potassium iodide, so that Johnson's method of analysis is not discredited.

The failure of their x-ray measurements (7) to show any lines other than those due to potassium iodide is difficult to understand and the experiments should be repeated employing analysed samples under very carefully controlled conditions, for, as has been shown earlier, the triiodide decomposes at a low temperature, and potassium iodide is the solid decomposition product.

OTHER SOLVATED POLYIODIDES

Other solid solvated polyiodides of the alkali metals are known: $KIBr_2 \cdot H_2O$, $NaICl_4 \cdot 2H_2O$, $LiICl_4 \cdot 4H_2O$, and $HICl_4 \cdot 4H_2O$ (a hydrogen polyhalide) have been reported by Wells and Weeler (8), Cagliotti (9), Cremer and Duncan (10), and others. The first two of the above polyhalides have been shown to exist in both the hydrated and anhydrous states, while the hydrogen compound and the polyiodides of potassium appear to exist only in the solvated state (i.e., the combined solvent appears to be essential for the existence of these compounds in the solid state). In view of these solvated polyhalides it seemed of interest to investigate further the alkali polyiodides which have been reported in the literature, paying particular attention to the possibility of solvation and the conditions which favor the formation of such solvated compounds.

THREE SOLID POLYIODIDES OF CESIUM

Two solid polyiodides of cesium have been prepared from water solution and their composition studied by Wells and his associates (11) and others. One compound was definitely shown to be the triiodide, while the other was first believed to be a pentaiodide. Briggs, Greenawald, and Leonard (12a), and Briggs (12b) from studies of the ternary system iodine–cesium iodide–water, and of the binary system iodine–cesium iodide have shown the higher polyiodide to be a tetraiodide (CsI_4) and not a pentaiodide.

Rae (13) from a study of the rate of loss of iodine from a fused mixture of iodine and cesium iodide, over sodium hydroxide, finds a sharp change in the loss curve when the composition of the solid corresponds with CsI_4.

Abegg and Hamburger (14) studied the ternary system iodine–cesium iodine–benzene at 25°C., employing methods similar to those adopted with potassium iodide. Three ternary invariant solutions were found which were considered to be in equilibrium with (1) CsI and CsI_3, (2) CsI_3 and CsI_5 (or CsI_7) (3) CsI_5 (or CsI_7) and CsI_9. These results, while agreeing with those of other workers for the triiodide, *disagree regarding the composition of the polyiodide intermediate in iodine content, and an enneaiodide is reported, which has not been found by other investigators.*

The experimental data from which Abegg and Hamburger deduce the composition of the intermediate polyiodide are in reality in favor of this compound being a tetraiodide rather than a penta-or hepta-iodide. In their table 12 (15) the most concentrated ternary invariant (0.563 *N*) was shown to exist in equilibrium with solids whose composition might be varied between $CsI_{4.8}$ and CsI_9. When the solid phase had reached the composition of the enneaiodide no further change in its composition was noted while the solution was raised to 1.04 *N* (saturation with respect to iodine being 1.09 *N*). This indicates cesium enneaiodide as the highest polyiodide present at the invariant 0.563*N*. This invariant was, however, obtained when the solid phase had a composition $CsI_{4.8}$, which indicates that the intermediate polyiodide contains less iodine than a pentaiodide (since no mixture of CsI_9 and CsI_5 could produce a composition of $CsI_{4.8}$). Their tables 13 and 14 (reference 14, pages 423 and 424) are similar, and show that at the next lower invariant (0.170 *N*) the two solids present are CsI_3 and a compound richer in iodine than the triiodide. These experiments therefore indicate that the intermediate polyiodide contains more iodine than a triiodide and less than a pentaiodide—i.e., is a *tetraiodide*, which agrees with the conclusions of Briggs and his associates.

Abegg and Hamburger appear to have been influenced in the interpretation of their own results regarding the composition of this polyiodide, partly by the work of Wells and his coworkers (8), who had reported a pentaiodide, and also by the analogy with rubidium and potassium (since they had obtained heptaiodides of these two metals). They therefore assumed that the cesium compound must be either a penta- or hepta-iodide, without considering the possibility of a tetraiodide. Indeed a tetrahalide does not seem probable, for in the analogous compounds the total number of halogen atoms is odd—e.g., CsI_3, $CsBr_3$, $CsIBr_2$, $CsICl_2$, $CsICl_4$, etc.; this tetraiodide is the first compound which apparently contains an even number. Although Rae (16) has reported evidence indicating the existence of cesium tetrabromide, Cremer and Duncan (17) in experiments similar to those of Rae found no evidence for a polybromide[3] more complex than $CsBr_3$. Considering the apparent uniqueness of the tetraiodide it seemed desirable to study it further and in particular to determine whether it contained combined solvent (as this seemed a possible explanation of its unusual composition), and at the same time to check the tri- and ennea-iodides.

PREPARATION OF CESIUM IODIDE

Cesium chloride was prepared from finely ground pollucite, following the procedure described by Harned and Schupp (18). The chloride was converted to the acid sulfate by heating strongly with sulfuric acid in a platinum dish. The sulfate was removed by the addition of the calculated quantity of freshly recrystallized $2BaI_2 \cdot 15H_2O$. Evaporation of the filtrate yielded cesium iodide, which was further purified by one recrystallization from water. This product was dried, at first gently and then at 200°C., and ground to a powder. Duplicate analyses (as silver iodide) gave an iodine content corresponding to 99.81 and 99.87 per cent of that of pure cesium iodide.

CESIUM TRI- AND TETRA-IODIDES

Samples of cesium tri- and tetra-iodides were prepared from water solution by the methods outlined by Briggs, Greenawald, and Leonard (12a). Samples of each, plus a minimum quantity of mother liquor, were placed in weighing bottles and loss of moisture over phosphoric oxide determined. In each case a steady loss (about 0.1 gram per day) was maintained as long as mother liquor was present and then the loss dropped suddenly to practically nothing (0.0002 gram per day) at which point specimens were analyzed for moisture by the complete method described earlier (1). The results in neither case showed more than 0.10 per cent moisture to be present, which indicates that these two polyiodides exist unsolvated and that they do not form stable hydrates. The mean of two analyses for the higher polyiodide gave CsI, 40.68 per cent, polyiodide I_2,

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[3] Since this work was completed Harris (J. Chem. Soc. **1932**, 1694) has demonstrated the existence of the interesting compound $2KBr_6 \cdot 3H_2O$, which contains an even number of halogen atoms.

59.24 per cent (0.08 per cent H_2O); and a CsI to I_2 ratio of 1:1.49, which is in good agreement with $CsI \cdot 1.5\ I_2$.

THE SYSTEM IODINE–CESIUM IODIDE–BENZENE AT 25°C.

Experiments were carried out in a manner similar to those with potassium iodide (reference 1, page 605), with the exception that the containing bottles were not rotated, but merely immersed up to the neck in a thermostat; the lack of stirring, caused by the absence of rotation, did not appear to materially affect the rate of attainment of equilibrium, since rate of reaction at the solid liquid interphase seems to be the governing factor in this respect. The state of subdivision of the solid phase was found to be the chief factor influencing the rate of reaction. The alkali iodide was therefore ground to a very fine powder before the experiments were commenced.

TABLE 1

The formation of solid polyiodides of cesium by the removal of iodine from benzene solution

DAYS	NORMALITY	DAYS	NORMALITY
Experiment No 1 CsI, 3 04 grams	Benzene, 50 cc I_2, 7 05 grams	Experiment No 2 CsI, 2 01 grams	Benzene, 100 cc I_2, 16 57 grams
0 2	0 950	7	0 936
11	0 475	12	0 872
18	0 435	19	0 812
24	0 415	25	0 782
36	0 400	40	0 740
50	0 399*	55	0 710
		70	0 705*
Experiment No 3 CsI, 2 00 grams	Benzene, 50 cc I_2, 12 50 grams		
12	0 770		
22	0 747		
33	0 743*		

* Equilibrium value

The invariant solutions in equilibrium with the solid phases (1) CsI, CsI_3 and (2) CsI_3, CsI_4 were redetermined and values of 0.00338 N and 0.170 N, respectively, obtained at 25°C. These values are almost identical with those obtained by Abegg and Hamburger. ($N/100$ thiosulfate was employed in determining the lower value).

Table 1 (see also figure 1) contains the data concerning the preparation of the cesium polyiodides. In experiment 1 when equilibrium was established the solid phase had a composition $CsI \cdot 1.5\ I_2$ (by synthesis), while in experiments 2 and 3 the solid phase present at equilibrium had an iodide to iodine ratio very close to 1:4.0. Samples of each of the polyiodides prepared in this manner were placed in isoteniscopes (described earlier) and the benzene pressures maintained at 25°C. determined. Neither the tri- nor the tetra-iodide maintained a constant benzene pressure, while analyses of the samples showed no combined benzene to be present. The tetraiodide gave CsI 40.32 per cent and polyiodide iodine 59.52 per cent, or $CsI:1.51\ I_2$, which confirms the composition of the unsolvated tetraiodide. The enneaiodide, on the other hand, maintained a constant benzene pressure of 32 mm., showing the presence of combined benzene. This pressure was maintained until nearly all the benzene had been removed, for as soon as the pressure fell appreciably analysis showed the sample to contain 99.8 per cent iodine plus iodide.

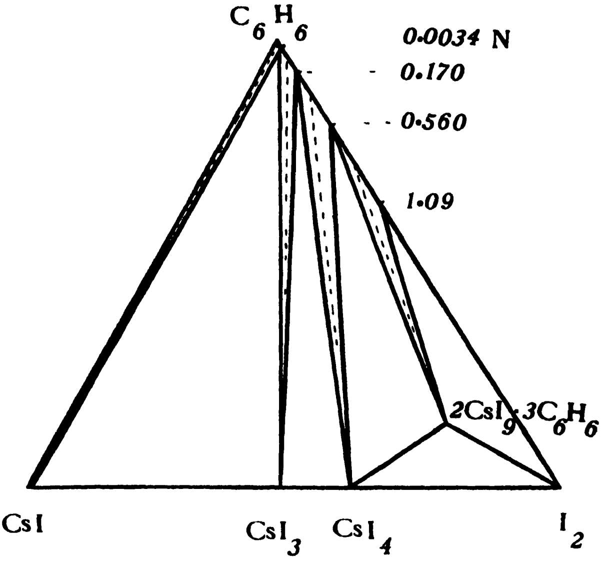

Fig. 1

To determine the number of molecules of combined benzene, samples of the enneaiodide were placed in isoteniscopes and benzene slowly removed until the constant pressure of 32 mm. was first reached, and then the isoteniscopes were opened and the samples rapidly transferred for analysis. Five analyses on the two preparations of the enneaiodide (experiments 2 and 3, table 1) gave concordant results, indicating this compound to have the composition $CsI_9 \cdot 1.5C_6H_6$, i.e., $2CsI_9 \cdot 3C_6H_6$. Two typical analyses, by the usual method, gave for the per cent of CsI, 18.61 and 18.65, mean 18.63; polyiodide iodine 73.58 and 73.26, mean 73.42 and (by difference) 7.95 per cent benzene; this corresponds with $CsI:4.03I_2:1.42C_6H_6$.

These results support the existence of two unsolvated polyiodides of cesium, CsI_3 and CsI_4, and the enneaiodide solvated with benzene. The equilibrium conditions at 25°C. of these three compounds in the ternary system in which benzene is the solvent are indicated in figure 1.

SOLID POLYIODIDES OF RUBIDIUM

Wells and Wheeler (8) prepared rubidium triiodide from aqueous solution, while Foote and Chalker (19), from a study of the ternary system iodine–rubidium iodide–water at 25°C. found only the triiodide. Abegg and Hamburger (14) studied the ternary system iodine–rubidium iodide–benzene at 25°C. and found three invariant solutions which they considered to be in equilibrium with (1) RbI and RbI_3, (2) RbI_3 and RbI_7, and (3) RbI_7 and RbI_9 respectively. From analogy with the results obtained with cesium and potassium it seemed most probable that the rubidium hepta- and ennea-iodides, which had not been reported in the aqueous system, would be found to contain combined benzene, and that they owed their existence to this fact.

TABLE 2

The preparation of polyiodides of rubidium at 25°C.

DAYS	NORMALITY	DAYS	NORMALITY
Experiment No. 1 RbI, 0.80 gram	Benzene, 50 cc. I_2, 3 50 grams	Experiment No 3 RbI, 1 30 grams	Benzene, 50 cc. I_2, 12 54 grams
10	0.400	11	1 070
20	0.400*	18	1 050
		25	1.030
Experiment No. 2 RbI, 1.188 grams	Benzene, 50 cc. I_2, 9 02 grams	35	1 025
		50	1 023*
3	0.900		
10	0.804		
17	0.774		
30	0.768		
40	0.767*		

* Equilibrium value.

Rubidium iodide of reagent quality was obtained from Hopkins and Williams and an attempt was made to prepare the three polyiodides reported by Abegg and Hamburger, employing a method similar to that used in the case of $2\ CsI_9 \cdot 3C_6H_6$ (details in table 2). In experiment No. 1 at equilibrium the solid phase consisted of RbI and I_2 in the ratio 1:1.00, i.e., RbI_3. Some of this material in an isoteniscope maintained no constant benzene vapor pressure, while analysis showed no combined benzene. (By analysis this solid had the composition $RbI \cdot 0.99I_2$.)

Experiments 2 and 3 (table 2) are in agreement with the results of Abegg and Hamburger and indicate rubidium hepta- and ennea-iodides, respectively, as the solid phases present at equilibrium. Measurements at 25°C.

showed these two compounds to have very nearly the same benzene dissociation pressures, being 61.5 and 60.0 mm., respectively; however, measurements over a temperature range indicated that these two compounds had independent dissociation pressure curves. From the equilibrium diagram, figure 2, it is seen that the heptaiodide, on the removal of benzene, breaks down into triiodide plus enneaiodide, which accounts for the heptaiodide having the higher benzene dissociation pressure at 25°C., although at this temperature it has the lower iodine dissociation pressure.

Combined benzene was determined by difference by the usual method. For the heptaiodide were found RbI, 18.52 and 18.67, mean 18.59; I_2, 68.40 and 68.71, mean 68.55; total 87.14; benzene, 12.86 per cent; this corresponds with RbI:3.08I_2:1.88C_6H_6, or $RbI_7 \cdot 2C_6H_6$. The enneaiodide gave on analysis RbI, 15.53 and 15.31, mean 15.42; I_2, 73.12 and 73.68, mean 73.40; benzene, 11.18 per cent; this corresponds with RbI:3.98I_2: 1.97C_6H_6 or $RbI_9 \cdot 2C_6H_6$.

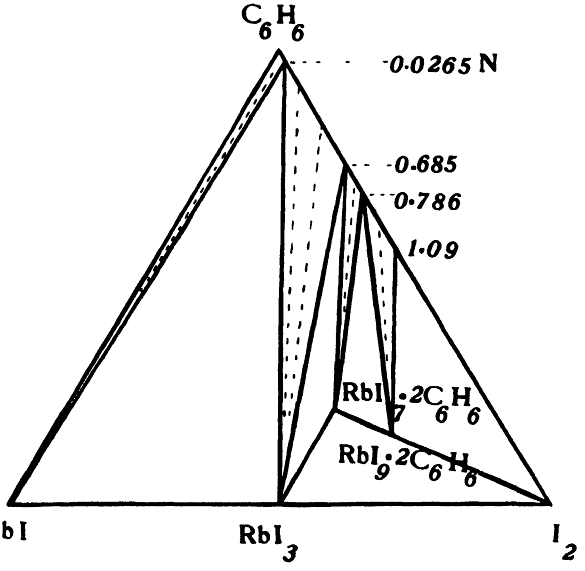

FIG. 2

The invariant solutions when (1) RbI_3 and $RbI_7 \cdot 2C_6H_6$ and (2) $RbI_7 \cdot 2C_6H_6$ and $RbI_9 \cdot 2C_6H_6$ were the solid phases, were redetermined and mean values of 0.680 and 0.782 respectively obtained, which do not agree too well with 0.690 and 0.790 *N* of Abegg and Hamburger. We may take a mean of the two different sets of observations as the best values which would give 0.685 and 0.786 *N*.

These results indicate three solid polyiodides of rubidium, one unsolvated, RbI_3, and two solvated with benzene, $RbI_7 \cdot 2C_6H_6$ and $RbI_9 \cdot 2C_6H_6$.

The equilibrium conditions of these compounds at 25°C. are shown in figure 2.

The results obtained indicate the existence of *only three unsolvated* polyiodides of the alkali metals, the triiodides of rubidium and cesium and a tetraiodide of the latter. This shows the tetraiodide to be the highest unsolvated polyiodide formed by the alkali metals at 25°C.

POTASSIUM ENNEAIODIDE

The results obtained with rubidium and cesium confirm Abegg and Hamburger that enneaiodides of these two metals exist at 25°C. (both compounds containing combined benzene). Abegg and Hamburger consider the heptaiodide to be the highest polyiodide of potassium stable at 25°C. and indeed give some evidence that an enneaiodide does not exist; however, a close examination of their work shows that their experiments were not sufficiently critical to justify a definite conclusion on this point.

The existence of enneaiodides of cesium and rubidium suggested that a similar compound of potassium might be formed. In one experiment containing 1.66 grams of potassium iodide, 16.16 grams of iodine, and 50 cc. of benzene, the normality of the solution (after approaching equilibrium for two months) was 1.03, so that the solid present had an iodide to iodine ratio of 1 to 3.9, while the same material gave on analysis (mean of three) KI, 11.53, I_2, 72.56, and benzene (by difference) 15.90 per cent, which corresponds with $KI:4.11I_2:2.94C_6H_6$ or $KI_9 \cdot 3C_6H_6$. This material at 25°C. had a benzene dissociation pressure of 52 mm.

The composition of this polyiodide agrees with that obtained by Foote and Bradbury (20). Foote and Bradbury found only one solid ternary compound $KI_9 \cdot 3C_6H_6$ in the system iodine-potassium iodide-benzene at 25°C. and 6°C.; however, the author has obtained some evidence indicating two ternary compounds. The strongest evidence in favor of two ternary compounds comes from dissociation pressure measurements where two different constant benzene pressures were observed on removal of benzene (one at 52 mm. and the other at 50 mm. at 25°C.). Further work is necessary on this point.

It should be mentioned that the experimental method employed by Foote and Bradbury, where they used glass beads or porcelain chips which in a shaker greatly hastened attainment of equilibrium, is probably superior to the method of the author, for they found equilibrium attained in three days (or less) whereas in the work described here often a matter of a month or more was necessary and even then one could not be quite sure that true equilibrium was actually reached, the difficulty being greatest in dealing with the equilibrium conditions of the most complex polyiodides.

POLYIODIDES OF SODIUM AND LITHIUM

The work of Abegg and Hamburger (14), in which neither solid sodium nor lithium iodide remove iodine from a nearly saturated solution of iodine in benzene at 25°C., indicates that no solid polyiodides of these two metals, either unsolvated or solvated with benzene, exist at this temperature. From the general trend of the polyiodides of the metals of higher atomic weight it is not surprising to find no unsolvated polyiodides of either sodium or lithium (since there appear to be none of potassium, one of rubidium, and two of cesium). However, potassium enneaiodide solvated with benzene is just a little more stable than that of rubidium, so that it would appear significant that this stability is not continued with sodium or lithium.

In dilute solution the presence of sodium triiodide has been deduced by J. S. Carter (21) at 25°C., while in more concentrated solutions higher polyiodides are considered also to be present. In our study an aqueous solution, saturated with both sodium iodide and iodine at 25°C., was evaporated slowly. Two distinct types of crystal separated; the one less dense than the solution was shown to be $NaI \cdot 2H_2O$, while the other which was more dense was iodine alone. Similar results were obtained with lithium iodide. These experiments indicate that any polyiodides present in solution at 25°C. are not stable in the solid phase. Possibly one might express this another way by saying that at 25°C. the stable form of sodium and lithium hydrated polyiodides may be not solid but liquid. This viewpoint is supported by the fact that $KI_3 \cdot H_2O$ begins to melt at about 31°C.; so that above 31°C. and atmospheric pressure solid potassium triiodide would not be found. Consequently, experiments with sodium iodide were tried at lower temperatures where it was thought that a hydrated polyiodide might be stable in the solid phase.

TABLE 3

Analyses of sodium triiodide

TEMPERATURE OF PREPARATION	SOLID PLUS ADHERING MOTHER LIQUOR			MOTHER LIQUOR		
	NaI	I_2	H_2O	NaI	I_2	H_2O
degrees C						
10 6	30 40	53 80	15 79	30.15	53 45	16 31
10 6	30 32	53 81	15 90	30 10	53 41	16 51
11 6	31 02	53 47	15 63	30 42	53 72	15 89
11 6	31 12	53 40	15 53	30 42	53 72	15 89
Theory for $NaI_3 \cdot 4H_2O$	31 51	53 36	15 13			

An aqueous solution saturated with both sodium iodide and iodine was gradually cooled from room temperature; little change was apparent till a temperature of 11.8°C. was reached, when the solution became filled with fine blue-black needles, while the temperature remained nearly constant. By first cooling the solution down to 12°C. and removing any iodine or sodium iodide which separated, it was found possible to prepare a fairly homogeneous sample of the needles. After being freed as much as possible from mother liquor (the complete removal of mother liquor being impossible due to its viscosity and the very fine nature of the crystals) the needles melted almost completely at 11.8°C. The analyses (by complete method) for some preparations are given in table 3.

These results show that at 11.6°C. mother liquor and the solid separating have very nearly the same composition; however the solid is slightly richer in sodium iodide and poorer in water content. The mean composition of the solid separating at 11.6°C. corresponded to $NaI:1.02I_2:4.18H_2O$, which is quite close to $NaI_3 \cdot 4H_2O$.

Definite proof of the existence (and composition) of solid hydrated sodium polyiodides was sought in a phase rule study at 0°C. This study was attempted without using a mechanical shaker because of the difficulties involved at that temperature and since the equilibrium solutions were very much less concentrated than in the case of potassium polyiodides it was hoped that shaking would be unnecessary; however, equilibrium in the solutions richest in iodine was approached too slowly to permit an accurate study in the time available. The results obtained are therefore not quantitative, but in a qualitative manner support the existence of at least one solid polyiodide of sodium at 0°C., the composition of which is possibly $NaI_3 \cdot 4H_2O$.

Similar even more preliminary experiments with lithium iodide indicated the existence of at least one solid hydrated polyiodide of lithium which melts about 10°C. The results with sodium and lithium, while not being sufficiently definite to stand alone, are of interest since they fit in well with the trend shown by the polyiodides of the alkali metals of higher atomic weight, for potassium forms low-melting hydrated polyiodides, while rubidium and cesium form no such hydrated compounds. In this connection one might be permitted to speculate regarding the existence of polyiodides of hydriodic acid. Their existence in solution has been demonstrated by many workers. In the solid state, however, none have been isolated. Considering the general behavior of the polyiodides of the alkali metals one might predict that at a very low temperature solid hydrated polyiodides of hydrogen may be isolated.

ENNEAIODIDES THE HIGHEST POLYIODIDES

Enneaiodides of potassium, rubidium, and cesium have been kept in contact with iodine solutions in benzene which are nearly saturated (1.09 *N*) without any indication of a polyiodide higher than an enneaiodide being formed. However, in the nearly saturated solutions it would be difficult to detect a slow change. The evidence is therefore not quite conclusive, but indicates strongly that the enneaiodides are the most complex solid polyiodides of these three metals under the above conditions.

The work of Stromholm (22), Geuther (23), Chattaway and Hoyle (24), and others, seems to show that enneaiodides are the highest solid polyiodides of the quaternary ammonium salts such compounds as $N(CH_3)_4I_9$, $N(C_2H_5)(CH_3)_3I_9$ and $N(C_2H_5)_4I_7$ being reported. These compounds are also of interest in that they are apparently unsolvated (although no complete analyses are given), while the higher polyiodides of the alkali metals do not exist unless they contain combined solvent molecules. This difference between polyiodides of the alkali metals and those of the quaternary ammonium salts may be explained on the *hypothesis of relative ionic size.* This hypothesis (discussed in detail in a later publication) suggests that in ionic crystals (both ions monovalent) one of the factors influencing stability is relative ionic size—greater stability occurring when anion and cation are nearly equal in radius rather than when they are very unequal. In the substituted ammonium polyiodides there is a large cation (e.g., $N(CH_3)_4^+$) and also a large anion I_9^-, whereas in unsolvated polyiodides of the alkali metals there would be a very great difference between a small metal ion (K^+) and the very large I_9^- ion. This difference in size might be more or less made up by the packing of benzene molecules around the cation. This hypothesis is supported by CsI_9 containing one and one-half, RbI_9 two, and KI_9 three molecules of benzene, so that the smaller the cation the greater the number of benzene molecules. However, sodium and lithium (which ions usually most readily form solvated compounds) do not form stable polyiodides solvated with benzene. This failure of sodium and lithium would indicate that the formation of polyiodides solvated with benzene by the other alkali metals did not occur through the formation of covalent links between alkali ion and benzene molecules, but that the benzene molecules are only necessary to fill in the space lattice. Energies of formation of these compounds have been measured by dissociation pressure methods and found to be very nearly zero, which is further evidence that the benzene present is merely filling in the space lattice, i.e., that these solid polyiodides (solvated with benzene) are *lattice compounds.*

This study shows that potassium (as is usual) occupies a position intermediate between rubidium and cesium on the one hand and sodium and lithium on the other. For potassium forms solid polyiodides solvated with either water or benzene (none unsolvated), rubidium and cesium form polyiodides both unsolvated and solvated with benzene (none with water), while sodium and lithium probably form (at temperatures below 12°C.) solid polyiodides solvated with water (none unsolvated or solvated with benzene at 25°C.). In the interpretation of these differences there are two distinct factors to be considered: (a) the size or mass of the alkali ion,

(b) the nature of the solvent. It is not inconceivable that some such method as this may be of use in studying the properties of different solvents. An x-ray study of those polyiodides containing benzene would be useful and might lead to interesting results.

SUMMARY

1. At 25°C. and 1 atmosphere there are only three true binary polyiodides of the alkali metals, RbI_3, CsI_3, and CsI_4; the tetraiodide of cesium is the most complex binary compound.

2. The other solid polyiodides of the alkali metals reported have been shown to contain combined solvent and the presence of solvent is essential for the existence of these polyiodides in the solid state.

3. Ternary compounds in the systems iodine–alkali iodide–benzene have been shown to be: $2CsI_9 \cdot 3C_6H_6$, $RbI_9 \cdot 2C_6H_6$, $RbI_7 \cdot 2C_6H_6$ and that of the highest polyiodide of potassium $KI_9 \cdot 3C_6H_6$. The most complex ternary compounds appear to be enneaiodides.

4. Neither sodium nor lithium form solid polyiodides, unsolvated or solvated with water or benzene at 25°C., while evidence is presented that at temperatures lower than 25°C. these two metals probably form solid polyiodides solvated with water.

5. At 25°C. potassium forms solid polyiodides solvated with either water or benzene (none unsolvated), rubidium and cesium form polyiodides both unsolvated and solvated with benzene (none with water), while sodium and lithium probably form solid polyiodides solvated with water (at temperatures below 12°C.) and none unsolvated or solvated with benzene.

6. It is suggested that these differences may be correlated with (a) relative ionic size and (b) the nature of the solvent (third component).

The author wishes to express his sincere gratitude to Professor H. B. Baker, C.B.E., D.Sc., F.R.S., for his kindly interest during the work and to Mr. G. H. Cheeseman, B.Sc., for valuable suggestions. Grateful acknowledgment is made of a Beit Scientific Research Fellowship, during the tenure of which the experimental part of this paper was carried out.

REFERENCES

(1) Grace: J. Chem. Soc. **1931**, 594.
(2) Reference 1, page 596.
(3) Bancroft, Scherer, and Gould: J. Phys. Chem. **35**, 764 (1931).
(4) Reference 3, page 772.
(5) Reference 1, page 602.
(6) Reference 3, page 774.
(7) Reference 3, page 778.
(8) Wells and Wheeler: Z. anorg. Chem **1**, 442 (1892).
(9) Cagliotti: Atti accad. Lincei **9**, 563 (1929).
(10) Cremer and Duncan: J. Chem. Soc. **1931**, 2243.

(11) Reference 8, pages 86 and 442.
(12) (a) BRIGGS, GREENAWALD, AND LEONARD: J. Phys. Chem. **34**, 1951 (1930).
(b) BRIGGS: J. Phys. Chem. **34**, 2260 (1930).
(13) RAE: J. Phys. Chem. **35**, 1800 (1931).
(14) ABEGG AND HAMBURGER: Z. anorg. Chem. **50**, 422 (1906).
(15) Reference 14, page 423.
(16) RAE: J. Chem. Soc. **1931**, 1578.
(17) CREMER AND DUNCAN: J. Chem. Soc. **1931**, 1865.
(18) HARNED AND SCHUPP: J. Am. Chem. Soc. **52**, 3886 (1930).
(19) FOOTE AND CHALKER: Am. Chem. J. **39**, 561 (1908).
(20) FOOTE AND BRADBURY: J. Phys. Chem. **36**, 673 (1932).
(21) CARTER: J. Chem. Soc. **133**, 2227 (1928).
(22) STRÖMHOLM: J. prakt. Chem. **66**, 423, 517 (1902); **67**, 345 (1903).
(23) GEUTHER: Ann. **240**, 66 (1887).
(24) CHATTAWAY AND HOYLE: J. Chem. Soc. **124**, 654 (1923).

A NEW METHOD FOR OBTAINING DATA FOR THE SORPTION OF VAPORS BY SOLIDS

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A technique for obtaining sorption data more simply and rapidly than those ordinarily used has been developed for the sorption of vapors by solids. It arose by following up an idea suggested by two sentences found in papers by Cude and Hulett (1) and by Tryhorn and Wyatt (2), respectively. Cude and Hulett filled charcoal with water to get the pore space, not the sorption. Tryhorn and Wyatt noticed that the weight of benzene in charcoal when the visible liquid surface had just disappeared by evaporation was the same as that obtained by exposure to fully saturated vapor. However, the significance of their results is left uncertain, since in both cases capillary liquid might equally well have been present. The only test would be to compare the values obtained by wetting and superficial drying of so microporous a body as charcoal with values obtained for the sorption isotherm for distinctly unsaturated vapor. The same comment applies to any powder.

EXPERIMENTAL METHOD

The solid was placed in a commercial microfilter tube[1] with a sintered glass filter from which the excess liquid could be removed by suction or by centrifuging. As the liquid must be introduced on to the evacuated solid, the filter, A in figure 1, was placed in a bulb B with a ground glass joint C to the stopcock D through which the liquid could be introduced. The bulb and tube with stopcock was joined to the vacuum line by a ground glass joint E.

About a gram of the material to be used was placed in the filter and in certain cases washed with water, which was removed by suction and centrifuging. Weighings were taken of the bulb, tube, and filter separately and of the filter and the solid material. The solid was evacuated with heating by an electric furnace around the lower part of the bulb. The tube and bulb were detached at E and weighed, giving the weight of the evacuated solid. The liquid to be introduced was placed in the upper part of the tube and slowly admitted through the stopcock. In order to prevent the liquid from washing any stopcock grease down on to the solid, the lower bulb was cooled and the upper tube warmed so that the liquid vaporized into the bulb and condensed on the solid in the lower part of the bulb. When the solid was covered with liquid, the bulb was opened at C, the filter removed, and the excess liquid centrifuged off. In certain cases suction was applied for a few seconds to remove liquid from the sintered glass. The filter with the solid and the sorbed liquid was weighed in a weighing bottle and from these values the amount sorbed at saturation was calculated. An isotherm was determined by evacuating to a definite pressure and reweighing. The solid could be reëvacuated and the experiment repeated with the same or other liquids.

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[1] Jena Geräte glass, size 12, porosity 4, 1 centimeter inside diameter, Fish-Schurman Corporation, New York City.

TABLE 1

Maximum amount of various liquids retained at 23°C. by dehydrated chabasite in the centrifugal method

SUBSTANCE	x/m	CUBIC CENTIMETERS PER GRAM	MOLECULAR VOLUME
Water . .	0 323	0 324	18
Formamide	0 088*		33
Formic acid	0 473†	0 386	37
Methyl alcohol	0 268‡	0 339	40
Ethylene oxide .	0 056		49
Methyl cyanide.	0 048		51

* Mean of 0.078, 0.099, and 0 087.
† Mean of 0.485 and 0.461.
‡ Mean of 0 268, 0 272, 0 270, and 0.263.

EXPERIMENTS WITH CHABASITE[2]

It was most interesting to begin with a crystalline solid containing no pores in the ordinary sense of the word. The zeolites (3) are hydrated calcium aluminum silicates which can give up their water of hydration on evacuation or heating without destroying the crystal form of structure. The spaces left by the water may be filled indifferently by any molecule small enough to enter. They then form, as McBain (4) pointed out and as is now generally accepted, almost perfect molecular sieves or semipermeable membranes of great regularity. Evans (5) quotes Taylor (6) to the effect that the water molecules in chabasite lie on non-intersecting triagonal axes of the cubic space group. No other atoms lie on these axes, so there are long channels passing through the structure wide enough to accommodate fairly large molecules and empty of everything but water molecules.

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[2] $CaAl_2Si_4O_{12}\cdot 6H_2O$ subject to slight variation due to base exchange. Theory gives 21 3 per cent of water, but G Friedel (Bull soc franç. minéral. **22**, 5 (1889)) found 22 28 per cent

The chabasite crystals were washed with water before weighing, as in the routine described. It was found that evacuation for twenty-four hours at 350°C. brought the chabasite to constant weight at 10^{-6} cm. of mercury. The average of nine values gave 24.4 per cent of water lost by the chabasite. Expressed as ratio of weight of water to weight of dehydrated chabasite, $x/m = 0.323$. The results with liquids are summarized in table 1.

As is seen from table 1, the two substances with the largest molecular volume are taken up only to a small fraction of the extent of water, methyl alcohol, and formic acid. The small amount of formamide indicates that mere molecular volume is not the sole determining factor. The shape and composition of the molecule must also be of importance.

Formic acid has a small molecular volume, but it also attacks the chabasite and a deposit is observed on the filter. A sample of chabasite, used first with formic acid, was used again with water, which it took up to the extent of 28.5 per cent as compared with the original 24.4 per cent. This enlargement of the sorption space is fully adequate to account for the higher value of formic acid sorbed.

The heat of sorption of methyl alcohol by chabasite is considerable, the filter and glass bulb being observed to heat up to above 60°C., a much greater effect than was observed with charcoal and far too great to be explained as heat of compression.

Rapid sorption of methyl alcohol vapor by chabasite disintegrates the crystals to a powder, owing to the sudden unequal heating and expansion.[3] The heat on rapid sorption may decompose the alcohol and change the colorless crystals to yellowish-black. It was found impossible to desorb all the alcohol, and if the temperature were raised above 400°C. during evacuation, the crystals became yellow or black.

EXPERIMENTS WITH CHARCOAL

The charcoal was highly active (82 per cent)[4] air and steam activated charcoal made from especially pure sugar. It was covered with two thicknesses of silver foil pierced with fine holes and was evacuated for several days at 500°C. and 10^{-5} cm. of mercury. The volumes of liquid sorbed at 28°C. at saturation pressure or just below were 0.59 cc. of benzene, 0.6 cc. of water, and 0.61 cc. of acetic acid per gram of charcoal.

ISOTHERMS

It is possible to obtain isotherms by this method, especially on desorption, as a manometer in the vacuum system gives the pressure after partial

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[3] Compare the observation of M. G. Evans (Proc. Roy. Soc. London **A134**, 97 (1931)) on the disintegration by ammonia vapor.

[4] One gram of 200 mesh charcoal sorbs in three minutes from 50 cc. of a 0.2 *N* aqueous solution of iodine in 0.27 *N* potassium iodide, 82 per cent; method of N. K. Chaney, A. B. Ray, and A. St. John (Ind. Eng. Chem. **15**, 1244 (1923)).

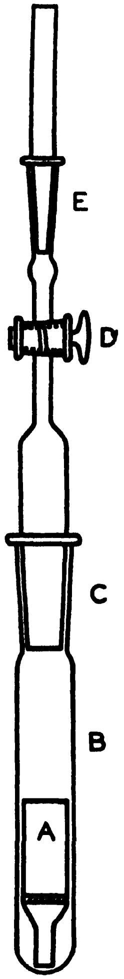

Fig. 1

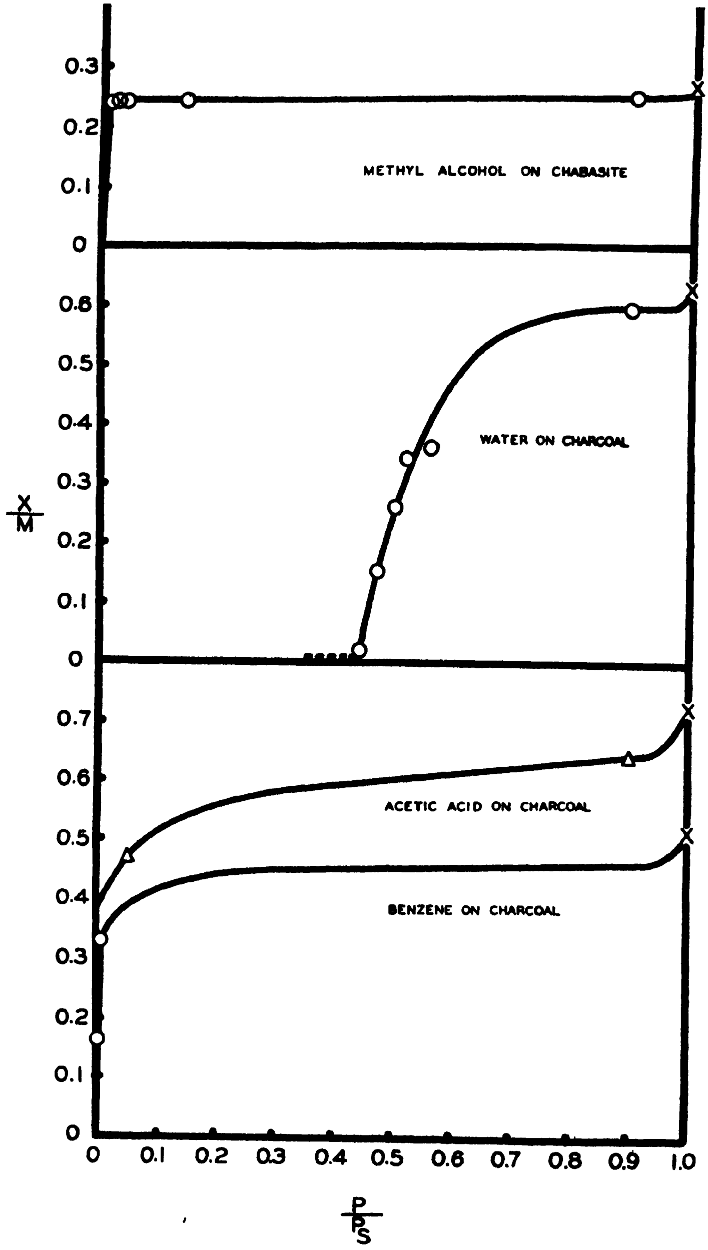

Fig. 2

Fig. 1. The Filter Tube Apparatus for Measuring Sorption
Fig. 2. Isotherms by the Filter Tube Method

evacuation, and at any stage the stopcock in the tube may be closed and the bulb, tube, and filter removed and weighed without exposing the solid to the atmosphere.

The results are shown in figure 2. Inspection of the isotherms for methyl alcohol and the crystalline chabasite reveals the ideal form of isotherms for uniform "surfaces."[5] It is even more rectangular than those obtained with highly evacuated, active charcoal (7). Here, therefore, is most definite proof of persorption and not condensation of capillary liquid. The isotherms for acetic acid and benzene on charcoal likewise show that sorption is far advanced at infinitesimal pressures.

The isotherms for the sorption of water by charcoal are of a wholly different type, owing to formation of a two-dimensional liquid permeating the charcoal, the water molecules being held as much by mutual polarization as by attachment to the charcoal (8). Comparison of these isotherms with those for organic vapors on the same charocal shows them to be due to sorption, or rather persorption, in both cases and that the isotherms with water cannot be interpreted as measuring the volume and distribution of the assumed pores of the charcoal. Inspection of the extreme right hand of each diagram in figure 2 shows the small additional amount of liquid held by capillary condensation in each case, an amount which is only a minute fraction of the total sorption.

SUMMARY

A simple method for the rapid and moderately accurate study of sorption of liquids and vapors by solids is described. Sorption isotherms obtained with a molecular sieve, dehydrated chabasite, are nearly rectangular, even more so than those for organic vapors with highly activated charcoal where the sorption goes largely to completion at infinitesimal pressures. The sorption of water, although of a different type, is likewise interpreted as persorption and definitely not as capillary condensation.

In conclusion my thanks are due to Professor J. W. McBain at whose suggestion this work was undertaken.

REFERENCES

(1) CUDE, H. E., AND HULETT, G. A.: J. Am. Chem. Soc. **42**, 398 (1920), footnote 1.
(2) TRYHORN, F. G., AND WYATT, W. F.: Trans Faraday Soc. **22**, 137 (1926).
(3) For more complete references and discussion, see McBain, J. W.: The Sorption of Gases and Vapours by Solids, Chapter V, page 167. George Routledge and Sons, Ltd., London (1932).

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[5] A. S. Coolidge (J. Am. Chem. Soc. **49**, 712 (1927), figure 3) has published a very similar result, ascribed to J. C. Woodhouse, for the sorption of water by chabasite.

(4) McBain, J. W.: Colloid Symposium Monograph **4**, 1 (1926); Kolloid-Z. **40**, 1 (1926).

Schmidt, O.: Z. physik. Chem. **133**, 280 (1928).

(5) Evans, M. G.: Proc. Roy. Soc. London **A134**, 97 (1931).

(6) Taylor, W. H.: Z. Krist. **74**, 1 (1930). See also Pauling, L.: Proc. Nat. Acad. Sci. **16**, 453 (1930).

(7) McBain, J. W., Lucas, H. P., and Chapman, P. F.: J. Am. Chem. Soc. **52**, 2668 (1930).

McBain, J. W., Jackman, D. N., Bakr, A. M., and Smith, H. G.: J. Phys. Chem. **34**, 1439 (1930).

McBain, J. W., and Britton, G. T.: J. Am. Chem. Soc. **52**, 2198 (1930).

(8) For much further evidence, see McBain, J. W., Porter, J. L., and Sessions, R. F.: Communicated to J. Am. Chem. Soc.; also reference 3, p. 143.

THE INTERACTION OF ETHYL ALCOHOL AND OXYGEN PHOTOSENSITIZED BY HYDROGEN PEROXIDE

A CONTRIBUTION TO THE HABER-WILLSTÄTTER MECHANISM OF ENZYME REACTIONS

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For the enzymotic oxidation of ethyl alcohol, Haber and Willstätter (1) postulate the following mechanism:

$$CH_3CH_2OH + \text{Enzyme} = CH_3.\overset{/}{C}H(OH) + \text{Monodesoxy-enzyme} + H^{\cdot} \qquad \text{(a)}$$

$$CH_3\overset{/}{C}H(OH) + CH_3CH_2OH + O_2 = 2CH_3CHO + OH + H_2O \qquad \text{(b)}$$

$$OH + CH_3CH_2OH = CH_3\overset{/}{C}H(OH) + H_2O \qquad \text{(c)}$$

Some light may be thrown upon the possibility of such a mechanism by a study of the effect of the introduction of OH radicals into an aqueous alcohol solution in the presence of oxygen. If the postulated mechanism is the correct one, the chain would then be started at step (c) and the reaction continue as a chain reaction. Since Haber and Willstätter also give a similar mechanism for the oxidation of acetaldehyde in which the OH radical is again the active link in the chain,

$$CH_3CHO + \text{Enzyme} = CH_3\overset{/}{C}O + \text{Monodesoxy-enzyme} + H^{\cdot} \qquad \text{(a')}$$

$$CH_3\overset{/}{C}O + CH_3CHO + H_2O + O_2 = 2CH_3COOH + OH \qquad \text{(b')}$$

$$OH + CH_3CHO = CH_3\overset{/}{C}O + H_2O \qquad \text{(c')}$$

it is to be expected that the oxidation of the acetaldehyde formed in the alcohol oxidation will occur as a secondary process.

One convenient method for introducing OH radicals is to decompose photochemically hydrogen peroxide which has been added to the alcohol solution. The question as to whether the first step in the hydrogen peroxide decomposition is the formation of OH or of HO_2 is not pertinent in this connection (2). In either case OH is ultimately one of the products of the decomposition. If HO_2 is formed in the first step, OH is formed in the next step.

$$HO_2 + H_2O_2 = H_2O + OH + O_2$$

The evidence will tend to favor the mechanism of Haber and Willstätter if the oxidation process under these conditions is found to be a chain reaction.

EXPERIMENTAL

The apparatus used has been described elsewhere (3). It consisted of a quartz reaction vessel mounted on a horizontal shaker running at 265 oscillations per minute, immersed in a water thermostat. With the exception of those for the determination of the temperature coefficient, all runs were made at 25 ± 0.05°C. The reaction vessel was connected by a short piece of suction tubing to a Hulett gas burette (4) filled with water. The source of illumination was a horizontal, air-cooled, laboratory model, Hanovia mercury arc operating at 60 ± 1 volts and 4 ± 0.05 amperes mounted outside the thermostat directly in front of a quartz window in the side of the thermostat.

The general procedure was to fill the apparatus with oxygen, add 25 to 30 cc. of the liquid sample to the shaker, shake a few minutes until temperature equilibrium was attained, and then to start the reaction by removing the shutter from in front of the quartz window. Tank oxygen was used. The hydrogen peroxide was obtained by diluting "Superoxol" with water. Since check runs using 95 per cent alcohol obtained by diluting absolute ethyl alcohol with water gave the same rates of reaction as those made with commercial 95 per cent ethyl alcohol, the commercial alcohol was used in the experiments without further purification. Unless otherwise specified, all data refer to 95 per cent ethyl alcohol.

When the reaction products were to be determined, the liquid product was removed from the shaker, diluted to 250 cc. with water, and analyses made on aliquot portions. The amount of acid was determined by titration with 0.05 *N* NaOH, peroxide by titration with 0.1 *N* thiosulfate of the iodine liberated from acid potassium iodide solution, and aldehyde by the Ripper method (5) after the solution from the determination of peroxide had been made neutral with sodium hydroxide solution. Appropriate blank analyses were made in every case.

RESULTS

Photochemical oxidation of alcohol

It was first necessary to determine if alcohol itself was oxidized photochemically in the presence of oxygen. Reports in the literature by various workers differ on this point. Several workers (6) have found that alcohol and oxygen do not react when illuminated, while Dhar and Sanyal (7) report that a small amount of acetaldehyde was formed when moist alcohol and oxygen were exposed to sunlight for an hour. In some preliminary experiments made with an aged, water-cooled Kromayer mercury arc, it was found that no appreciable amount of oxygen was taken up on illuminating alcohol with oxygen over a period of ten hours. When the Hanovia lamp was used as a source of illumination, however, the absorption of oxygen was marked, as shown by curve A of figure 1. The analysis of the product is given in table 1. The product gave a blue color with chromic acid and ether. Since Clover and Richmond (8) have shown that neither peracetic acid nor organic peroxides give this test, hydrogen peroxide must have been formed in the oxidation. All attempts to find peracetic acid according to the method of D'Ans and Frey (9) and to that described by

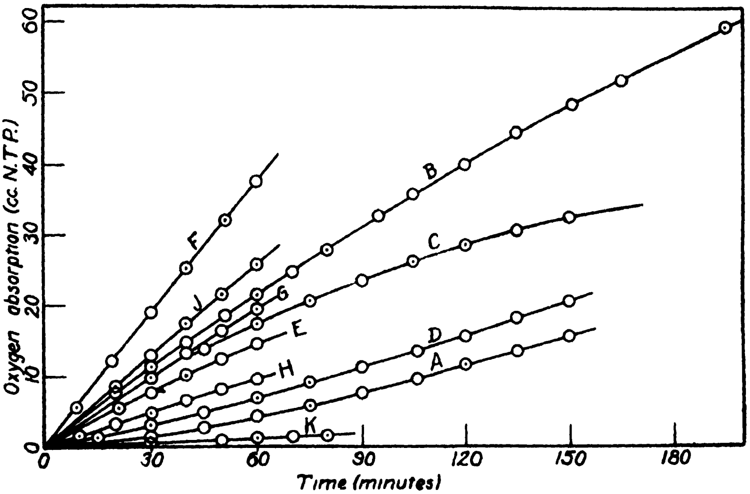

FIG. 1. RATE OF OXIDATION OF ETHYL ALCOHOL

A. 25 cc. alcohol.
B. 25 cc. alcohol and 0.81 millimole hydrogen peroxide.
C. B − A.
D. 25 cc. alcohol and 1.98 millimoles acetaldehyde.
E. 25 cc. alcohol and 0.48 millimole hydrogen peroxide.
F. 25 cc. alcohol and 4.75 millimoles hydrogen peroxide.
G. 25 cc. alcohol, 4.75 millimoles hydrogen peroxide, and 0.074 millimole ethylamine.
H. 25 cc. alcohol, 4.75 millimoles hydrogen peroxide, and 0.74 millimole ethylamine.
J. 25 cc. 50 per cent alcohol and 4.75 millimoles hydrogen peroxide.
K. 25 cc. alcohol and 0.74 millimole ethylamine.

Backstrom (10) gave negative results. As may be seen from the rate curve, the rate was autocatalytic in nature. To determine if this increasing rate were due either to the accumulation of acetaldehyde or of acetic acid, runs were made with alcohol to which had been added acetaldehyde and acetic acid separately in quantities comparable to those formed in the oxidation with alcohol alone. The rate with added acetic acid was practically the same as with alcohol alone, while, as may be seen from curve D, figure 1, the rate with added acetaldehyde is somewhat faster, but is also increasing with time. As before, hydrogen peroxide was identified in the product. The autocatalytic rate, therefore, is probably due to the formation and accumulation of hydrogen peroxide.

Oxidation of alcohol photosensitized by hydrogen peroxide

In order to be sure that the photochemical oxidation of alcohol with added hydrogen peroxide was a true photosensitized process and not one of direct oxidation of the alcohol by the peroxide, it was necessary to show that hydrogen peroxide, alcohol, and oxygen do not react unless illuminated. Although Renard (11) had shown that such a reaction does not occur, the reaction was tried using 0.81 millimole of hydrogen peroxide and 25 cc. of alcohol without illumination. No appreciable absorption of oxygen was noted over a period of eight hours.

TABLE 1

Analyses of products (millimoles)

	A 25 CC ALCOHOL	B 25 CC ALCOHOL + 0.81 MILLIMOLES HYDROGEN PEROXIDE	C 25 CC ALCOHOL + 1.98 MILLIMOLES ACETALDEHYDE
Acid..	0.39	2.10	0.58
Aldehyde .	0.60	2.01	2.07
Peroxide	0.14	0.50	0.25
Oxygen absorbed	0.70	2.95	0.92

When alcohol–hydrogen peroxide solutions were illuminated, the rate of oxygen absorption was rapid (curves B, E, and F of figure 1) and decreased with time. As shown in column B of table 1, the amount of peroxide found in the product was less than that initially added.

With 4.75 millimoles of added hydrogen peroxide, the rate of oxygen absorption was not so fast with 50 per cent alcohol solution as it was with 95 per cent alcohol solution (compare curves F and J of figure 1).

The determination of the rates of reaction with 4.75 millimoles of added peroxide at 0°, 25°, and 35°C. gave temperature coefficients for this reaction of 1.06 and 1.13 per 10° rise.

Effect of inhibitors on the alcohol oxidation

Chain reactions are characterized by the marked decrease in rate produced by the addition of small quantities of inhibitors. For this reason, the effect of inhibitors on the reaction was studied. The addition of 0.74 millimole of ethylamine decreased the rate of the photochemical oxidation of alcohol in the absence of peroxide to about one-fourth (curve K, figure 1) and 2.2 millimoles of benzene reduced it to about one-half.

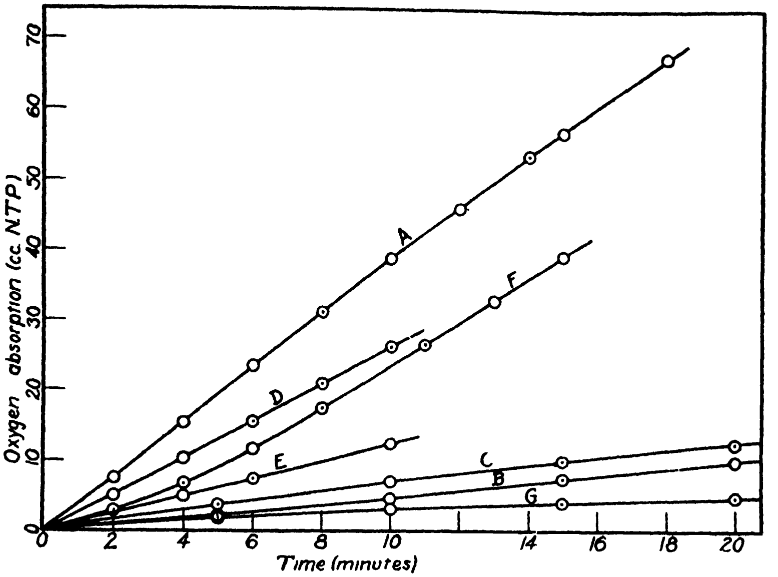

FIG. 2 RATE OF OXIDATION OF AQUEOUS ACETALDEHYDE SOLUTIONS

A. 25 cc. 10 per cent acetaldehyde.
B. 25 cc. 1 per cent acetaldehyde.
C. 25 cc. 1 per cent acetaldehyde and 0.9 millimole hydrogen peroxide.
D. 25 cc. 10 per cent acetaldehyde and 1 cc. 95 per cent alcohol
E. 25 cc. 10 per cent acetaldehyde and 5 cc. 95 per cent alcohol
F. 25 cc. 10 per cent acetaldehyde and 0.074 millimole ethylamine.
G. 25 cc. 10 per cent acetaldehyde and 0.74 millimole ethylamine.

As curves F, G, and H of figure 1 show, the addition of 0.07 millimole of ethylamine to 25 cc. of alcohol solution containing 4.75 millimoles of hydrogen peroxide reduced the rate to about one-half, while the addition of 0.74 millimole of ethylamine reduced the rate to about one-fourth of its original value.

Using 0.95 millimole of hydrogen peroxide in 25 cc. of alcohol, the addition of 0.1 millimole of benzylamine reduced the rate to about one-fifth and 0.5 millimole of benzylamine reduced the rate to about one-tenth of its original value. Like quantities of hydroquinone, ethylamine, diphenylamine, and benzene were found to exhibit similar inhibitory effects.

When the oxidation with 0.95 millimole of hydrogen peroxide was allowed to proceed for about an hour before the inhibitor was added, the rate was markedly retarded as before, but in this case the rate slowly increased until it had practically reached its original value at the end of another hour.

Oxidation of aqueous acetaldehyde solutions

The photochemical oxidation of aqueous acetaldehyde solutions was studied in order to determine what effect the acetaldehyde formed might have on the alcohol oxidation. With 25 cc. of a 10 per cent (by volume) solution, the rate of oxidation was very rapid (figure 2). The addition of 0.9 millimole of hydrogen peroxide did not increase the rate. With a 1 per cent solution of acetaldehyde, the rate was much slower. In this case the addition of 0.9 millimole of hydrogen peroxide did increase the rate.

Ethylamine and ethyl alcohol inhibited the oxidation, the alcohol being much less efficient as an inhibitor than the amine (figure 2).

DISCUSSION

Since no photochemical oxidation of alcohol was noted when the Kromayer lamp was used, but a marked reaction found with the Hanovia lamp, the variation in the results reported by different workers on the photochemical oxidation of ethyl alcohol may probably be ascribed to differences in the intensities of the light sources used.

Curve C of figure 1 was obtained by subtracting curve A from curve B and represents, therefore, the amount of oxygen absorption due to the added 0.81 millimole of hydrogen peroxide. This curve may be seen to be approaching an asymptotic value of some 40 cc. of oxygen, which is equivalent to about 1.8 millimoles. Since the ratio of moles of oxygen absorbed to moles of hydrogen peroxide used is greater than two, this result indicates a minimum chain length greater than one, assuming that two OH radicals are obtained from each hydrogen peroxide molecule decomposed and that every OH initiates a chain. These assumptions obviously may be incorrect, but such a calculation does give a minimum value for the chain length. If the first step in the hydrogen peroxide decomposition is HO_2, the minimum chain length is then increased by a factor of four. At the time when the slopes of curves A and B become equal, the concentration of hydrogen peroxide will have reached a steady state at which its rate of formation is equal to its rate of decomposition.

Since ethylamine absorbs light only very weakly and that in a region between 2190 and 2480 Å. (12), the possibility that the inhibitory action of this substance might be due to a light screening effect is excluded.

Furthermore, the effect cannot be due to a destruction of the hydrogen peroxide by the amine because of the large ratio of the amount of peroxide present to that of the amine (4.75 to 0.074). Such marked decrease in rate of reaction can only be due to the existence of a chain reaction. The amount of inhibition is not great enough, however, to indicate a long chain. This conclusion is concordant with the previous calculation of minimum chain length. The observation that no retardation occurs when an otherwise efficient inhibitor is added to the system after reaction has proceeded for some time is not new (13). Such behavior is usually ascribed to the formation during the oxidation of peroxides which destroy the inhibitor.

The fact that the addition of 0.9 millimole of hydrogen peroxide to a 10 per cent solution of acetaldehyde did not increase the rate of oxidation is as one would expect. Since acetaldehyde has a high absorption coefficient over a wide range (14), one would expect the hydrogen peroxide to be well screened in such a concentrated solution of acetaldehyde. That the rate of oxidation of the 1 per cent solution is increased by the addition of peroxide indicates that, at this concentration, some of the light is being absorbed by the hydrogen peroxide molecules which decompose and enter into the oxidation. As shown by curves F and G of figure 2, the effect of ethylamine as an inhibitor is great. Curves D and E of figure 2 show that ethyl alcohol is an inhibitor of the aldehyde oxidation, but not a very good inhibitor. This fact explains why it is that the acetaldehyde formed in the alcohol oxidation is not immediately oxidized, but rather accumulates and may be identified in the product.

Bowen and Tietz (15) concluded that an organic peroxide, probably diacetyl peroxide, is formed when gaseous, liquid, or dissolved acetaldehyde is exposed in presence of oxygen to ultra-violet light, but that in aqueous solutions the peroxide will have reacted and disappeared at the end of twenty seconds. They also showed that the oxidation of acetaldehyde was a chain reaction and found that alcohol acted as an inhibitor when added to hexane solutions of acetaldehyde. From their results one would expect that, even if a peroxide were first formed in the oxidation of acetaldehyde in a 95 per cent aqueous alcohol solution, the peroxide would immediately react to form acetic acid which would be the oxidation product found.

All of the experimental evidence indicates that the oxidation of alcohol photosensitized by hydrogen peroxide is a chain reaction, but that the chains are short ones. It is of interest to note that Alyea and Bäckström (16) in their work on the inhibitory action of alcohols on the sodium sulfite oxidation found that their data could best be explained by assuming that if the oxidation of alcohol were a chain reaction, the chains were short ones. Under their experimental conditions the chain length of the alcohol oxidation would be even shorter than in the present case.

It is clear that these considerations do not prove that the Haber-Willstätter mechanism is correct. They do show, however, that the concept of a chain mechanism for the oxidation of ethyl alcohol is a justifiable one. Moreover, all of the experimental results reported in this paper may be satisfactorily interpreted by this mechanism.

SUMMARY

1. With an intense source of light, and in contact with oxygen, ethyl alcohol is oxidized photochemically, the process being auto-accelerating in nature.

2. The oxidation of alcohol by oxygen may be photosensitized by hydrogen peroxide.

3. Such an oxidation is a chain reaction with short chain length.

4. The photo-oxidation of aqueous acetaldehyde solutions is a chain reaction with longer chain length.

5. A chain mechanism such as that of Haber and Willstätter involving hydroxyl radicals as intermediates in the chain is compatible with the experimental results.

REFERENCES

(1) HABER AND WILLSTÄTTER: Ber. **64,** 2844 (1931).
(2) UREY, DAWSEY, AND RICE: J. Am. Chem. Soc. **51,** 1371 (1929).
ALLMAND AND STYLE: J. Chem. Soc. **1930,** 596, 606.
(3) ALYEA: Thesis, Princeton University.
(4) TAYLOR AND BURNS: J. Am. Chem. Soc. **43,** 1274 (1921).
(5) KINGSCOTT: Methods of Quantitative Organic Analysis, p. 118, Longmans, Green and Company, London (1914).
(6) CIAMICIAN AND SILBER: Ber. **46,** 3894 (1912).
SERNAGIOTTO: Atti accad. Lincei, **28,** I, 432 (1919); Chem. Abstracts **14,** 1672 (1920).
(7) DHAR AND SANYAL: J. Phys. Chem. **29,** 926 (1925).
(8) CLOVER AND RICHMOND: Am. Chem. J. **29,** 179 (1903).
(9) D'ANS AND FREY: Ber. **45,** 1848 (1912).
(10) BÄCKSTRÖM: Medd. Vetenskapsakad. Nobelinst. **6,** No. 15, 9 (1927).
(11) RENARD: Ann. chim. phys. [5] **16,** 289 (1880).
(12) BIELECKI AND HENRI: Compt. rend. **156,** 1861 (1913).
(13) WAGNER AND BRIER: Ind. Eng. Chem. **23,** 49, 662 (1931).
(14) BIELECKI AND HENRI: Compt. rend. **155,** 456 (1913).
(15) BOWEN AND TIETZ: J. Chem. Soc. **1930,** 234.
(16) ALYEA AND BÄCKSTRÖM: J. Am. Chem. Soc. **51,** 90 (1929).

THE AUTOXIDATION OF STANNOUS CHLORIDE. III

The Photochemical Reaction[1]

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In the preceding paper (1) the thermal reaction of stannous chloride with atmospheric oxygen was discussed, and evidence given to show that it is probably a thermal chain reaction similar to the autoxidation of sodium sulfite and of benzaldehyde, investigated by Bäckström (2) and Alyea and Bäckström (3). In order to secure further proof of the chain mechanism of the autoxidation of stannous chloride, the effect of visible and ultra violet radiation on the reaction was investigated.

APPARATUS

The apparatus used was similar to that used in the studies of the thermal reaction. A reaction flask was made from a quartz tube of 1¼ inches inside diameter, and 7 inches long. Indentations were made in the bottom, as was done with the glass flasks, to insure a better agitation. It was found impracticable to use a flask exactly like those of glass (1) with a bulb in the lower part. The quartz flask did not give a high enough area of gas-liquid interface to keep the solution saturated with oxygen and thus give the same reaction velocity as determined in the glass flasks, but it gave reproducible results, and thus allows a comparison of the results with positive catalysts and inhibitors.

The light source used was a capillary mercury vapor lamp of the type described by Daniels and Heidt (4). This lamp gives a high intensity in the ultra-violet region, and allows more accurate measurements than a low intensity lamp.

Some absorption measurements were made on the quartz monochromator described by Heidt and Daniels (5). Spectrograph work was done by means of a Krüss quartz spectrograph equipped with a single 60° prism.

ABSORPTION SPECTRUM OF STANNOUS CHLORIDE

Preliminary experiments having shown that ultra-violet radiation was effective in speeding up the autoxidation of stannous chloride, it was neces-

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sary to determine what wave lengths were active in causing this result. The absorption spectrum for the stock solutions of stannous chloride (32 grams per liter of $SnCl_2$; 0.8 N in HCl) was determined on the spectrograph, and it was found that the region of complete absorption extends up to 3000 Å. Decreasing the concentration of stannous chloride shifts the limit of complete absorption toward the lower wave lengths.

CORRECTION FACTOR FOR POLYCHROMATIC LIGHT

The monochromator was not suitable for the full set of experiments on quantum yield, using a shaken cell, and no filter could be arranged which would give a high transmission of the mercury line at 3020 Å. and still shut out all lines at 3130 Å. and higher, so that it was necessary to use polychromatic light in these experiments. The light intensity in the quantum yield experiments was determined by the use of the uranyl oxalate actinometer described by Leighton and Forbes (6). A weighted average quantum yield of 0.553 was calculated for the range of wave lengths used, from the data given in their article on quantum yields for monochromatic light. In the determination, the uranyl oxalate actinometer was shaken at the same speed in the same flask as was used for stannous chloride in order to give comparable results. Since the range of absorption of uranyl oxalate and stannous chloride is different it was necessary to determine a correction factor to be applied to the number of quanta obtained by the actinometer. This factor was obtained by the use of two similar quartz cells in series. The actinometer solution was placed in the second cell. The first cell was filled successively with distilled water and stannous chloride stock solution, and the decomposition of the actinometer solution measured in each case. The ratio of the number of quanta absorbed by the stannous chloride to the number absorbed by uranyl oxalate was found to be 0.62 ±0.01. This factor was applied to all the runs with different lamps, since Daniels and Heidt have shown (4) that the distribution of energy in the ultra-violet region varies only slightly with the voltage at a constant wattage.

TABLE 1

Effect of light intensity on quantum yield

I_0	ϕ
quanta per minute	
7 7 $(10)^{17}$	33
5 2	29
3 2	14
2 0	12

VARIATION OF QUANTUM YIELD WITH THE LIGHT INTENSITY

It is known that for many photochemical reactions the quantum yield ϕ varies with the intensity of the light. The variation in intensity was produced by different lamps and by varying the wattage of the lamps. Table 1 shows the effect on the quantum yield of the photochemical autoxidation of stannous chloride.

These intensities are given as the actual intensities causing reaction in the stannous chloride, that is, they are the actinometer intensities multiplied by the correction factor. The quantum yields are not accurate in the last figure, but two figures are given for comparison purposes.

The following sample of the calculations is given for reference.

Run No. 517

$$\begin{aligned}\text{"Light" reaction} &= \text{Total} - \text{"dark" reaction}\\ &= 7.86 - 0.86\\ &= 7.00 \text{ cc. of } O_2 \text{ used in 22 minutes}\end{aligned}$$

$$\frac{7.00}{22{,}400}\cdot\frac{716}{760}\cdot\frac{273}{298}\cdot\frac{2(6.06)\,(10)^{23}}{22} = 1.48(10)^{19} \text{ molecules of stannous chloride reacting per minute}$$

The actinometer solution decreased 2.80 cc. of 0.0328 *N* potassium permanganate in titer, after one hour exposure to the light.

$$\frac{(2.80)\,(0.0328)}{(1000)\,(60)\,(2)}\cdot\frac{(6.06)\,(10)^{23}\,(0.62)}{0.553} = 5.18(10)^{17} \text{ quanta per minute}$$

$$\phi = \frac{(1.48)\,(10)^{19}}{(5.18)\,(10)^{17}} = 28.6 \text{ molecules per quanta}$$

EFFECT OF CATALYSTS ON QUANTUM YIELD

If the thermal and photochemical reactions are completely analogous, accelerators and inhibitors should have the same effect on the photochemical reaction as on the thermal reaction. This is true for the catalysts used in the experiments. A few of the substances found to have pronounced effects on the thermal reaction were used, and gave the expected results as shown in table 2. It is to be noticed that picric acid, a strong inhibitor for the thermal reaction, reduces the quantum yield to almost exactly 1. The accelerators for the thermal reaction also accelerate the photochemical reaction as shown by the results. The last column of table 2 shows the relative effect of the catalysts used. In determining these values, the values for the quantum yield of the uncatalyzed reaction were interpolated from the results of table 1, expressed as a straight line proportionality between ϕ and I_0.

TABLE 2

Effect of catalysts on quantum yield

CATALYST	I_0	MOLECULES REACTING PER MINUTE	ϕ	PER CENT OF UNCATALYZED ϕ
	quanta per minute			
0.00002 *M* Picric acid	7.2 $(10)^{17}$	6.2 $(10)^{17}$	1	3
0.1 *M* Amyl alcohol	6.8	262	39	120
0.1 *M* Allyl alcohol	6.1	266	44	150
0.1 *M* Propionic acid	4.1	187	46	230
0.002 *M* Thiourea	3.2	83	26	160
0.065 *M* Hydroquinone	3.2	115	36	220
0.065 *M* Catechol	3.2	86	27	170
0.065 *M* Resorcinol	3.2	125	39	240
1.75 *M* Isopropyl alcohol	3.2	140	45	280
0.1 *M* *tertiary* Butyl alcohol	2.0	42	21	210

TABLE 3

Test of Beer's law for stannous chloride solutions

SOLUTION	CONCENTRATION OF STANNOUS CHLORIDE	CONCENTRATION OF HYDROCHLORIC ACID	PER CENT LIGHT TRANSMITTED	α
	grams per liter	*grams per liter*		
a	3.0	6.0	87.6	6.5
b	8.0	16.0	66.7	7.4
c	13.0	26.0	37.9	10.9
d	21.0	42.0	8.4	17.2
e	31.0	62.0	1.0	21.8

BEER'S LAW STUDIES FOR STANNOUS CHLORIDE

In general, light-absorbing media follow Beer's law, which gives the variation in absorption of a given wave length with varying concentration and thickness of the absorbing layer

$$\frac{I}{I_0} = e^{-\alpha c d}$$

Where I = the intensity of the transmitted light,
I_0 = the intensity of the incident light,
α = the molecular absorption coefficient,
c = the concentration (in moles per liter), and
d = the thickness of the layer.
(d = 1.3 cm. for the cell used).

Table 3 shows the results of these experiments on stannous chloride solutions. Hydrochloric acid was used to keep the stannous chloride from hydrolyzing, a constant ratio of hydrochloric acid to stannous chloride being used in all solutions. The wave length used was the 3130 Å. line, isolated by the use of the quartz monochromator. It can be seen that the value of α changes about threefold for a tenfold change in concentration of stannous chloride, showing that Beer's law does not hold. It was thus assumed that stannous chloride is not the absorbing medium. To test this hypothesis further, runs were made using a constant amount of stannous chloride with varying amounts of hydrochloric acid. The results are shown in table 4. In this case the value of α changes twelvefold for a thirty-sixfold change in the hydrochloric acid concentration. Hydrochloric acid alone shows no appreciable absorption at this wave length, so that the great change in α must be due to the influence of the hydrochloric acid on the stannous chloride. Thus the medium which absorbs the light quantum and becomes activated is not stannous chloride, nor the Sn^{++} ion, but must be some substance whose concentration *increases* with addition of hydrochloric acid to the system. The absorbing medium is thus either the complex chloro acid $HSnCl_3$ or H_2SnCl_4, or the ions $SnCl_3^-$ and $SnCl_4^-$ of those acids. That these complex ions are present in an acid solution was shown by Prytz (7).

TABLE 4

Effect of varying amounts of hydrochloric acid on the Beer's law constant

SOLUTION	CONCENTRATION OF STANNOUS CHLORIDE	CONCENTRATION OF HYDROCHLORIC ACID	PER CENT LIGHT TRANSMITTED	α
	grams per liter	*grams per liter*		
g	13.0	4.4	69.7	4.1
c	13.0	26.0	37.9	10.9
f	13.0	156.0	1.1	50.3

TABLE 5

Molecular absorption coefficient

Solution No. 10; 32.7 grams of stannous chloride per liter; 0.811 *N* hydrochloric acid

WAVE LENGTH	PER CENT LIGHT TRANSMITTED	α
2850 Å.	0.0	∞
3020	4.9	13.4
3130	28.4	5.6
3340	97.9	0.095
3650	100.0	0.0

MOLECULAR ABSORPTION COEFFICIENT

The molecular absorption coefficient was determined for a stannous chloride solution containing 32.7 grams of stannous chloride per liter and

0.811 *N* in hydrochloric acid, by use of the monochromator. Table 5 gives the results. These values of α are not applicable to other concentrations, because of the non-validity of Beer's law, but are included to show the range of partial and complete absorption.

SUMMARY

1. The autoxidation of stannous chloride is shown to be a photochemical chain reaction by the quantum yields of more than unity.
2. The photochemical and thermal reactions are affected similarly by accelerators and inhibitors; thus the hypothesis of a chain mechanism is supported for the thermal reaction.
3. Stannous chloride shows complete absorption below a certain limit; the limit is about 3000 Å. for the stock solutions used in the research, containing about 32 grams of stannous chloride per liter and being 0.8 *N* in hydrochloric acid, and is lower for more dilute solutions.
4. Stannous chloride was shown not to obey Beer's law. This was explained by the assumption that the complexes $HSnCl_3$ and H_2SnCl_4 are the active agents in absorbing the light, since the concentrations of these substances are increased by addition of hydrochloric acid to the system.
5. The molecular absorption coefficients for one stock solution are given, showing complete absorption of light at 2850 Å. and below, partial absorption from 3020 Å. to 3340 Å., and complete transmission at 3650 Å. and above.

REFERENCES

(1) Haring, Robert C., and Walton, James H.: J. Phys. Chem. **37**, 133 (1933).
(2) Bäckström, H. L. J.: J. Am. Chem. Soc. **49**, 1460 (1927).
(3) Alyea, H. N., and Bäckström, H. L. J.: J. Am. Chem. Soc. **51**, 90 (1929).
(4) Daniels, F., and Heidt, L. J.: J. Am. Chem. Soc. **54**, 2381 (1932).
(5) Heidt, L. J., and Daniels, F.: J. Am. Chem. Soc. **54**, 2384 (1932).
(6) Leighton, W. G., and Forbes, G. S.: J. Am. Chem. Soc. **52**, 3139 (1930).
(7) Prytz, M.: Z. anorg. Chem. **172**, 147 (1928).

MEASUREMENT OF THE RATE OF ADSORPTION AT CONSTANT PRESSURE

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In the simplified formula for the process of adsorption as suggested by Langmuir, the rate of the process is dependent upon the pressure of the gas being adsorbed. For the simple case of a single gas the rate of condensation may be given by (1)

$$+\frac{dx}{dt} = k_1p(1-\sigma)$$

and the rate of evaporation by

$$-\frac{dx}{dt} = k_2\sigma$$

Because of the importance of the measurement of the rate of adsorption in the determination of the activation energy (2) of the adsorption process, it was of interest to determine actually the significance of this pressure factor in the measurement. Most recent workers have used apparatus similar to that described by Pease (3). A quantity of gas is admitted and the velocity of adsorption is determined by the rate of pressure change. In one case reported the pressure actually decreased from 624 mm. to 235 mm. in 71 minutes. In the measurement of adsorption isotherms for which the process was devised, this change in pressure is of no consequence, since the process continues to equilibrium.

APPARATUS

The apparatus was constructed of Pyrex glass throughout and is illustrated in figure 1. Tube A containing the adsorbent was connected through a special stopcock with the gas burette E and manometer G. The traps B were cooled with solid carbon dioxide and ether. Capillary tubing was used except in the pump system. The manometer was arranged to act as a constant volume instrument and tungsten wire contacts were connected with a small electric light to serve as the indicator. The leveling bulb for the burette was supported by a wire over a pulley to a set of reducing gears. Thus the level of the mercury in the burette could be changed rapidly and with precision. In order to measure the rate of adsorption at constant pressure the manometer was adjusted to the reading for the pressure desired and the gas burette opened to the catalyst. The volume change of the process, at constant pressure, could be read directly from the burette each minute. By closing the burette after admission of the gas to be adsorbed this apparatus was also used to determine the adsorption at constant volume.

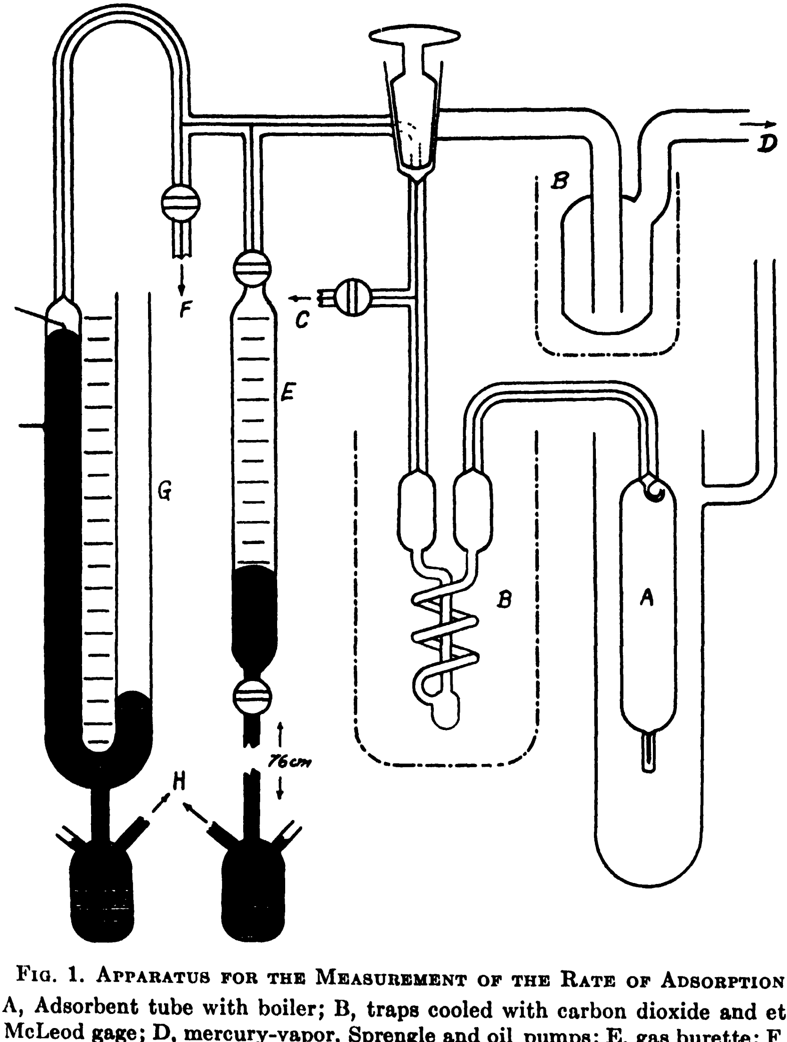

FIG. 1. APPARATUS FOR THE MEASUREMENT OF THE RATE OF ADSORPTION

A, Adsorbent tube with boiler; B, traps cooled with carbon dioxide and ether; C, McLeod gage; D, mercury-vapor, Sprengle and oil pumps; E, gas burette; F, gas reservoirs and purification; G, constant volume manometer with electric contact; H, leveling bulbs.

VARIATION OF RATE WITH PRESSURE

A mixed oxide catalyst, $MnO\text{-}Cr_2O_3$, was selected to illustrate the effect of pressure on the rate of adsorption. For comparison the material was prepared as described by Taylor and Williamson (4). The data presented in table 1 and figure 2 was obtained on 24 grams of the mixed oxides. Be-

TABLE 1

Adsorption of hydrogen on a mixed oxide catalyst

24 grams of $MnO\text{-}Cr_2O_3$ at 132°C

TIME	ADSORPTION NO 3 VOLUME CONSTANT		ADSORPTION NO 4 PRESSURE 480 MM	TIME	ADSORPTION NO 5 VOLUME CONSTANT	
	Pressure	Volume adsorbed	Volume adsorbed		Pressure	Volume adsorbed
	mm	*cc*	*cc*		*mm*	*cc.*
2	480	6 5	6 5		480	6 4
3	467	7 2	7 6		460	7 7
4	451	8 1	8 5		447 5	8 5
5	439	8 8	9 2		435	9 1
6	430	9 3	9 8		425	9 7
7	420	9 9	10 4		416	10 2
8	413	10 25	10 9		408	10 6
9	406	10 7	11 4		402	10 9
10	400	11 0	11 8		395	11 3
11	394	11 35	12 2		389	11 7
12	388	11 7	12 5		384	12 0
13	383	12 0	12 8		378 5	12 3
14	379	12 2	13 2		373	12 7
15	374	12 5	13 5		369	12 9
17	366	12 9	14 0		361	13 3
20	355 5	13 8	14 8		350	13 9
25	339 5	14 4	15 9		334	14 8
30	326	15 2	16 9		321	15 5
40	305	16 4	18 5		299 5	16 8
50	287 5	17 4	19 9		282	17 8
60	273	18 2	21 0		267 5	18 6
75	255	19 4	22 5		250 5	19 5
90	240	20 05	23 4	76	480	20 2
105	227 5	20 89	24 5	77		20 35
120	216 5	21 4	25 6	78		20 5
				79		20 7
				80		20 9
				82		21 1
				85		21 5
				90		22 0
				95		22 5
				100		23 0
				110		23 8
				120		24 6

fore the measurement of adsorption the sample was reduced at 350–370°C. for three days and evacuated twenty-four hours at 450–470°C. by means of mercury-vapor and oil pumps. After the determination of the inert space of the system with purified nitrogen, the material was again evacuated twenty-four hours at 450–470°C. A similar evacuation of twenty hours followed each adsorption measurement.

Adsorption No. 3 was carried out at constant volume by the method previously described to obtain the rate of adsorption. With all other conditions identical except that the pressure was maintained constant, curve 4 was obtained. It is quite evident that as the formula predicts, the adsorption at constant pressure continues at a higher rate than in those cases in which the pressure decreases. At the end of two hours in this case the difference is an increased adsorption of 4.2 cc. by the method advocated, amounting to 19 per cent of the total amount adsorbed by the former method in this length of time. A fifth adsorption was made in which the process was at constant volume during the first 75 minutes after which the pressure was increased immediately to 480 mm. and the adsorption measurements continued at that pressure. In this adsorption, curve 5, it was surprising to find the high rate at which after 75 minutes the adsorption increased toward the value previously obtained. After two additional adsorptions were made on the sample at 132°C. at constant pressure, which

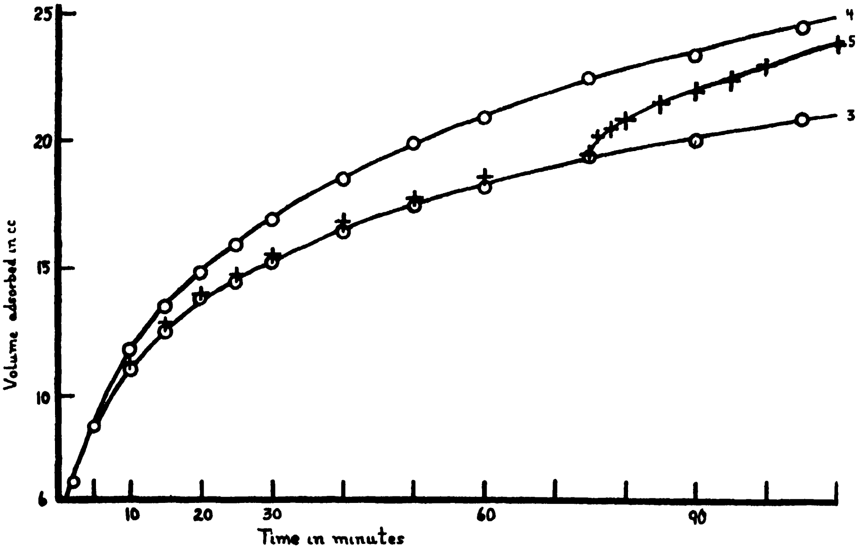

FIG. 2. RATE OF ADSORPTION

Curve 3 at constant volume; curve 4 at constant pressure in themselves agreed with number 4, similar results were obtained in adsorptions at 100°C. by the two methods.

STABILITY OF THE ADSORBENT SURFACE

Adsorbent surfaces are known to be highly complex. However the author has contended that by rigorously following a definite method of preparation and cleaning of the surface, reproducible results in a given sample should be obtainable. Two possible methods of determining whether a surface has been completely degassed are the use of the McLeod gage or the repetition of the evacuation and adsorption. The complete cleansing may of course result not in a surface of maximum activity but merely in one of constant activity. The McLeod gage was used previously (5) in the study of palladium to check the completeness of the degassing process. In the present study the amount of hydrogen adsorbed was less in the first two trials, table 2, than in the subsequent experiments. The method and time of each step of the process was identical throughout. Among the possible factors are the following. The extra evacuation after each adsorption may have finally removed all interfering materials, or the added period of heating during evacuation may have produced activating changes in the surface. The hydrogen adsorbed may have an activating effect upon the surface, cleansing it of other gases, or actually completing the reduction of the oxide. Burrage (6) has recently discussed the necessity of flushing the surface Whatever the process, it is evident that in the present case the surface reaches a maximum activity and remains quite constant. This final surface has a larger capacity than that of Taylor and Williamson (see table 3), although the samples agree with each other more

TABLE 2

TIME	ADSORPTION 1	ADSORPTION 2
minutes	*cubic centimeters*	*cubic centimeters*
2	3 9	5 9
30	11 9	14 5
60	14 6	18 3
120	17 8	22 6

TABLE 3

Amount of adsorption

SAMPLE	TAYLOR AND WILLIAMSON	1ST ADSORPTION	3RD ADSORPTION	5TH ADSORPTION
minutes	*cc per gram*	*cc per gram*	*cc per gram*	*cc per gram*
10	0 39	0 34	0 46	0 47
30	0 45	0 50	0 63	0 65
60	0 53	0 61	0 76	0 77

closely than the first and last adsorption on the present sample. It is perhaps superfluous to remark that this increased adsorption is produced by the same method as is used in producing the most active catalytic surface, i.e., by repeated reduction.

ACTIVATION ENERGY

Although the purpose of this determination did not involve the calculation of activation energies, they may be obtained from the data at the two temperatures. Since the rates at each temperature are different depending upon the method used, it is not surprising to find some variation in the value of E resulting. This activation energy of adsorption varies with the fraction of the surface covered, the first gas adsorbed requiring less activation than the final amount. The data as presented in table 4 have been calculated so that they may be compared with the data of Taylor and Williamson. The present sample weighed 0.51 as much as that of the former authors and therefore the volume interval 15–20 cc. corresponds to that between 7.8–10.3 cc. for an equal fraction of the surface covered in the present sample, etc.

TABLE 4

Activation energy in adsorption

Hydrogen on MnO–Cr_2O_3 at 100–132°C

VOLUME ADSORBED	E IN CALORIES PER MOLE ADSORBED	
	Pressure	Volume
cc		
7.8–10.3	4,580	10,300
10.3–12.9	6,700	14,000
12.9–15.5	9,800	15,400
15.5–18.1	12,600	

CONCLUSION

The Langmuir theory of the adsorption process requires that the velocity of condensation be dependent upon the pressure. This has been proven to be experimentally true in the case of hydrogen adsorbed upon the mixed oxides of manganese and chromium. As a result, in the determination of the activation energy of the adsorption process from rate measurements it is necessary that the method used shall consider the effect of pressure. A method is here suggested for this measurement at constant pressure, previous work having been done at constant volume. Repeated adsorptions upon the same surface were found to increase in rates to a maximum on the third adsorption. After this amount of use the surface remained constant during five additional adsorptions. The conclusion is that the surface should first be shown to be stable before it may be used to obtain data at various temperatures for calculation and comparison. This apparatus and method is also ideally suited for the direct determination of the adsorption isobar.

REFERENCES

(1) See TAYLOR, H. S.: Treatise on Physical Chemistry, Volume II, p. 1072. D. Van Nostrand Co., New York (1931).

(2) TAYLOR: J. Am. Chem. Soc. **53**, 578 (1931).

(3) PEASE: J. Am. Chem. Soc. **45**, 1196 (1923).

(4) TAYLOR AND WILLIAMSON: J. Am. Chem. Soc. **53**, 2168 (1931)

(5) TAYLOR AND MCKINNEY: J. Am. Chem. Soc. **53**, note 30, p. 3613 (1931).

(6) BURRAGE: Trans. Faraday Soc. **28**, 192 (1932). The Adsorption of Gases.

HEATS OF WETTING OF CELLULOSE ACETATE BY ALIPHATIC ALCOHOLS AND AROMATIC HYDROCARBONS[1]

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This paper is a further contribution to the study of the fine structure of cellulose ester plastics from the point of view of sorption (1). The energetics of sorption consist principally of heats of adsorption, wetting and swelling. In view of the polydisperse character of most of the cellulose colloids (2) it is quite possible that a swelling in a given liquid may consist of two acts, *viz.*, actual *solution* of a more disperse or lower molecular fraction, and wetting of a less disperse, higher molecular portion, which retains the gel structure. But at present we may regard heats of wetting and swelling as synonymous, with the proviso that later investigations may make necessary further differentiation.

Measurements have been made of the heat of wetting of an acetone-soluble cellulose acetate (40 per cent acetyl) in various non-solvent liquids at 25°C. The heat of wetting is defined as the calories of heat evolved per gram of dry acetate when the acetate is immersed in sufficient liquid to insure complete wetting.

Knoevenagel (3) measured the heat of swelling (wetting) of a cellulose acetate of 36.9 per cent acetyl in different mixtures of ethyl alcohol, benzene, and nitrobenzene. The heat of swelling in ethyl alcohol was about 650 calories per mole of cellulose acetate; in benzene, 1100 calories per mole; and in nitrobenzene, 1300 calories per mole.

The heats of wetting of various forms of cellulose (cotton, paper, wood) have been measured by Masson (4), Katz (5), Rosenbohm (6), Dunlap (7), and Barratt and Lewis (8).

EXPERIMENTAL

The heat of wetting was measured in a calorimeter consisting of a 1000-cc. Dewar flask fitted with a Beckmann thermometer, a stirrer, a heating coil, and a device for admitting the dry acetate similar to that used by Hedges (9) for measuring the heat of wetting of wool and silk. The calorimeter was packed in cotton in a cardboard box and the latter enclosed in an air thermostat at 25 ± 0.03°C. Five hundred cc. of liquid were used in each experiment and about 15 grams of dry cellulose acetate. The cellulose acetate was dried by heating twenty-four hours at 105°C. The acetate and liquid were kept in the thermostat for fifteen hours before mixing to insure equality of temperatures. In most cases the maximum temperature was attained within ten minutes. The cooling curve was followed for about twenty minutes. The heat capacity of the calorimeter was determined after each experiment by passing enough current through the calibrated heating coil to give about the same temperature rise as was observed in the wetting experiment. The required temperature corrections were made. The temperature rise varied from 0.15°C. to 1.00°C. The maximum deviation in check determinations was 5 per cent.

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[1] Communication No. 514 from the Kodak Research Laboratories. Presented at the Regional Meeting of the American Chemical Society held at Rochester, New York, February 6, 1932.

RESULTS

The results are shown in table 1. The first column gives the wetting liquids, the second column the molecular weight of the wetting liquid, and the third column the heats of wetting in calories per gram of dry acetate. The heat of wetting decreases with increase in molecular weight in a given homologous series. The time required for the maximum temperature rise (fourth column) may be taken as a measure of the rate of penetration of the liquid into the cellulose acetate. As would be expected, this time increases with increase in molecular weight in a given series.

TABLE 1

Heat of wetting of cellulose acetate

LIQUID	MOLECULAR WEIGHT	HEAT OF WETTING	TIME REQUIRED FOR MAXIMUM TEMPERATURE RISE	ADSORPTION BY SHEET FROM LIQUID AT 25°C		ADSORPTION BY FIBERS FROM SATURATED VAPOR AT 25°C	
				Weight per cent	Millimoles per gram	Weight per cent	Millimoles per gram
		calories per gram	*minutes*				
Water	18	6.01	3	13.7	7.6	14.3	7.94
Methyl alcohol	32	7.52	3			51.5	16.1
Ethyl alcohol	46	5.65	3	21.4	4.6	34.8	7.56
n-Propyl alcohol	60	4.94	6	21.2	3.5	25.6	4.27
n-Butyl alcohol	74	4.25	13	16.8	2.3	28.0	3.78
Benzene	78	7.57	8	22.1	2.8	39.1	5.01
Toluene	92	5.78	15	16.9	1.8	23.0	2.50
m-Xylene	106	3.69	30	5.0	0.5	17.1	1.61
Cyclohexane	84	1.40	10	1.5	0.18	12.6	1.50

Our value for the heat of wetting of the acetate in ethyl alcohol is 5.65 calories per gram of acetate or 1509 calories per mole, assuming a molecular weight of 267. This is much higher than Knoevenagel's value of 600 to 700 calories per mole. Likewise, our value of 7.57 calories per gram or 2021 calories per mole for the heat of wetting in benzene is higher than Knoevenagel's value of 1100. The difference in the acetyl contents of the cellulose acetates is not sufficient to account for the discrepancy.

The heat of wetting of the precipitated cellulose acetate by water is 6.0 calories per gram. The heat of wetting of a similar cellulose acetate in the form of a sheet is approximately 7 calories per gram as obtained by extrapolation from the integral heat of adsorption curve.

Knoevenagel (3) regarded his results as supporting a conception of definite (stoichiometric) solvate formation for the sorption of liquids by cellulose esters. Thus, in a previous communication (10) he claimed that "regularities of a molar character were found for the liquids taken up in swelling equilibrium with cellulose acetate." Thus in the swollen cellulose acetate obtained with varying mixtures of nitrobenzene–alcohol, acetic acid–benzene, or acetic acid–water, a constant value was obtained for the quotients:

$$\frac{\text{Moles adsorbed alcohol (benzene, water)}}{\text{Moles cellulose acetate}}$$

He now concludes that "to these molar relations" an unexpected, far-reaching addition for nitrobenzene is made,—"The amount of heat developed per mole or weight unit of cellulose acetate divided by the sum of the sorbed moles of liquid is constant." The constant in question is, surprisingly, the same for experiments with nitrobenzene–alcohol, alcohol–benzene, and benzene–nitrobenzene. The actual values are given in table 2.

TABLE 2

Values of H/A

LIQUID	MOLECULAR WEIGHT	*H* HEAT OF WETTING (SWELLING) IN KILOGRAM-CALORIES PER MOLE OF CELLULOSE ACETATE	*A* ADSORPTION IN MOLES PER MOLE OF CELLULOSE ACETATE	*H/A*
Alcohol	46	0.6 0.7	6.8 6.1	0.11 0.11
Benzene	78	1.1 1.1	9.9 9.8	0.11 0.11
Nitrobenzene	123	1.3 1.3	11.8 12.3	0.11 0.10

The "constancy" of the quotient H/A is good for these few substances. Our own values of heats of wetting do not bear out Knoevenagel's contention (see table 3).

TABLE 3

Values of H and A as found by the authors

LIQUID	HEAT OF WETTING	ADSORPTION	H/A
	calories per gram	*millimoles per gram*	
Water	6.01	7.9	0.76
Methyl alcohol	7.5	16.1	0.47
Ethyl alcohol	5.65	7.56	0.75
n-Propyl alcohol	4.94	4.27	1.16
n-Butyl alcohol	4.25	3.78	1.12
Benzene	7.57	5.01	1.51
Toluene	5.78	2.50	2.31
m-Xylene	3.69	1.61	2.29

Not only is the ratio of H/A quite inconstant, but our figures for the sorption, whether from liquid or saturated vapor, are of quite a different order from Knoevenagel's. This difference appears to be due chiefly to his experimental method, which involved measurement of liquid retained by precipitated cellulose acetate after centrifuging. This procedure does not appear to us likely to give correct values. In the case of complete solvents for cellulose esters, the existence of molecular compounds in certain cases (11) appears very probable, but in the case of sorption there does not appear to be any systematic evidence of stoichiometrical relations.

It was desired to obtain a relation between the heat of wetting and the corresponding amount of adsorption. It is not feasible to measure the adsorption by the precipitated material from the pure liquid but we can convert the precipitated acetate to a sheet, immerse it in the liquid, and weigh the amount sorbed after removing the excess from the surface. This sorption from the pure liquid by a sheet 0.005 inch thick is shown in columns five and six of table 1. The sorption of methyl alcohol could not be accurately measured in this way because of the evaporation during the handling of the sheet.

The sorption by the sheet, however, is probably less in most cases than that by the fibers under the same conditions, because of the smaller external surface of the sheet (12). Theoretically, the sorption by the fibers from the pure liquid should be the same as that by the fibers from the saturated vapor. Data for the latter obtained with a silica spring balance was shown in columns seven and eight of table 1. It will be seen that, with the exception of water, the sorption by the fibers from the saturated vapor is considerably higher than the sorption by the sheet from the pure liquid.

The sorption from the saturated vapor is composed partly of true surface adsorption and partly of capillary condensation but only the former contributes to the heat of wetting. It is, therefore, necessary to know how much of the sorption is surface adsorption and how much capillary condensation.

THE PORE VOLUME OF PRECIPITATED CELLULOSE ACETATE

Figure 1 shows the graph of the heat of wetting against the corresponding total sorption—assumed to be the same as that from the saturated vapor at the same temperature. In a previous communication (12) it was shown that the adsorption of the alcohols decreased with increase in molecular weight and appeared to become approximately constant at *n*-butyl alcohol. It was assumed that beyond this point there was no further capillary condensation. The curves of figure 1 indicate that capillary condensation in the alcohol series ceases at *n-propyl* instead of *n-butyl*, and in the aromatic hydrocarbon series at *toluene*. The prolongations of the lines through the origin enable us to determine the surface adsorption which is necessary to account for the heats of wetting of benzene and of methyl and ethyl alcohols. The excess sorption is due to capillary condensation and gives a measure of the pore volume filled by the liquid.

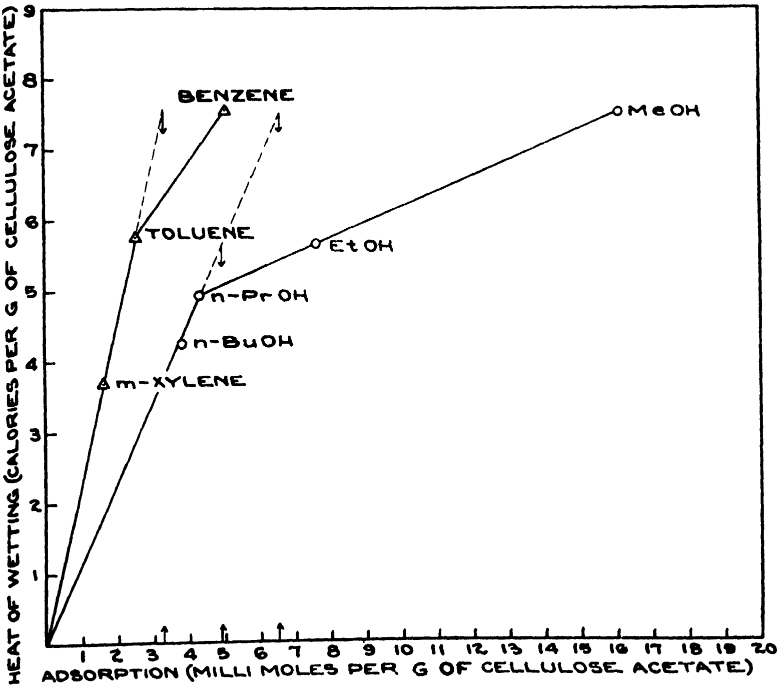

FIG. 1

Table 4 shows the surface adsorption and capillary condensation for the different liquids, together with the calculated pore volumes.

TABLE 4

LIQUID	SURFACE ADSORPTION	CAPILLARY CONDENSATION	DENSITY AT 25°C.	PORE VOLUME
	millimoles per gram	*millimoles per gram*		*cc per gram*
Methyl alcohol	6.52	9.58	0.7866	0.389
Ethyl alcohol	4.87	2.69	0.7851	0.158
n-Propyl alcohol	4.27	0.0		0.0
Benzene	3.28	1.73	0.8734	0.155
Toluene	2.50	0.0		0.0

Methyl alcohol gives the largest amount of capillary condensation. The pore volume thus occupied is 0.389 cc. per gram of dry acetate.

The straight lines through the origin in figure 1 correspond to a constant net heat of adsorption of 2.30 calories per millimole of adsorbed liquid for the benzene series, and 1.15 calories for the alcohol series.

SPECIFIC SURFACE AREA

Bartell and Fu (13) have described a method for the determination of the specific area of adsorbents based on the heat of wetting and adhesion tension. They have derived the equation

$$a = \frac{-Q}{A - KT\frac{dS}{dT}}$$

where a is the specific area, $-Q$ is the heat of wetting, A is the adhesion tension, S is the surface tension of the liquid, T is the absolute temperature, and $K = \frac{A}{S} = \cos \varphi$ where φ is the contact angle between solid and liquid. The contact angle betewen cellulose acetate sheet and water was found by Nietz (14) to be 25°. $S = 71.97$ dynes per centimeter and $\frac{dS}{dT} = -0.1474$.

Substituting in the above equation, $a = 2.4 \times 10^6$ sq. cm. We have previously obtained the value 5.9×10^6 sq. cm. from alcohol vapor adsorption data (12). This figure was obtained from the total molar adsorption at the saturation pressure and is possibly too high because of some capillary condensation of the higher alcohols.

SUMMARY

1. The heat of wetting of an acetone-soluble cellulose acetate by various non-solvent liquids has been measured at 25°C.
2. The respective amounts of surface adsorption and capillary condensation have been deduced from a comparison of the heats of wetting with adsorption data.
3. Calculations of pore volume and specific surface have been made.

REFERENCES

(1) Compare Sheppard, S. E., and Newsome, P. T.: J. Phys. Chem. **36,** 930 (1932).
(2) Compare McNally, J. G., and Godbout, A. P.: J. Am. Chem. Soc. **51,** 3095 (1929).
(3) Knoevenagel, E.: Kolloidchem. Beihefte **17,** 51 (1923).
(4) Masson, O.: Proc. Roy. Soc. London **74,** 230 (1904).
(5) Katz, J. R.: Proc. Acad. Sci. Amsterdam **13,** 958 (1911); **26,** 549 (1923).
(6) Rosenbohm, E.: Kolloidchem. Beihefte **6,** 177 (1914).
(7) Dunlap, M. E.: Forest Products Laboratory, Madison, Wisconsin, Proj. L-169.
(8) Barratt, T., and Lewis, J. W.: J. Textile Inst. **13,** T113 (1922).
(9) Hedges, J. J.: Trans. Faraday Soc. **22,** 178 (1926).
(10) Knoevenagel, E.: Kolloidchem. Beihefte **16,** 180 (1922).
(11) McNally, J. G., and Sheppard, S. E.: J. Phys. Chem. **35,** 2498 (1931).
Trogus, C., Tomonari, T., and Hess, K.: Z. physik. Chem. **B16,** 351 (1932).
(12) Sheppard, S. E., and Newsome, P. T.: J. Phys. Chem. **36,** 2306 (1932).
(13) Bartell, F. E., and Fu, Y.: Colloid Symposium Monograph **7,** 135 (1929).
(14) Nietz, A. H.: J. Phys. Chem. **32,** 255 (1928).

COMMUNICATIONS TO THE EDITOR

AN ATTEMPT TO SEPARATE ISOTOPES BY REVERSIBLE FRACTIONAL DISTILLATION[1]

This paper shows experimentally that the boiling points of the isotopic modifications of methylene chloride (CH_2Cl_2) differ by 0.005°C. or less. S. A. Peoples and L. Newsome (see Evans, Cornish, Lepkovsky, Archibald and Feskov: Ind. Eng. Chem., Anal. Ed., **2**, 342 (1930)) found no separation of the isotopes of chlorine by reversible fractional distillation of chlorobenzene, but their technique was improved for the present attempt, for which their 6.09 meter column was available.

Twenty liters of methylene chloride (Roessler and Hasslacher Co.) were carefully purified in the 6.09 meter column. Eighteen liters boiled within 0.1°C. or less, and this was returned to the cleaned still. The column was then operated at total reflux, and all traces of water very carefully removed from the condenser (in which any water collects). A calcium chloride tube was placed on the condenser vent. Water is sufficiently soluble in methylene chloride to reduce appreciably the specific gravity. Thirty cc. samples were now withdrawn at intervals for specific gravity tests, using a 25 cc. Leroy Weld type pycnometer (Central Scientific Co.), which made it possible to check individual weights of samples to less than 0.5 mg. The results, each being the mean of two determinations of $d^{25.10}_{25.10}$, are 1.32043 after 22 hours, 1.32039 after 64 hours, and 1.32046 after 117 hours (all at total reflux). The entire charge was then distilled off (all boiling within 0.1°C. or less), mixed, and found to have $d^{25.10}_{25.10}$ 1.32040. Values are not corrected for buoyancy of air.

Assuming Raoult's law, we write for the final limiting steady state at total reflux (Fenske: Ind. Eng. Chem. **24**, 483 (1932)):

$$X_{pA}/X_{pB} = \alpha^n X_A/X_B$$

where X_{pA}/X_{pB} is the ratio of the mole fractions of components A and B in the product, X_A/X_B is the same ratio in kettle, α is ratio of vapor pressure of pure A to that of pure B, and n is the number of theoretical plates. The 6.09 meter column used, packed with 4 mm. × 4 mm. cylindrical glass beads, should give a separation equal to that of at least forty theoretical plates, so that $n = 40$. (Evans, Cornish, Lepkovsky, Archibald, and Feskov: Ind. Eng. Chem., Anal. Ed. **2,** 342 (1930) and Peters: Ind. Eng. Chem. **14,** 476 (1922).) For methylene chloride at 39.7°C., its boiling point (Carlisle and Levine: Ind. Eng. Chem. **24,** 146 (1932)), dP/dT is 0.035 atmospheres per degree. (Morrison and Duus: Chem. & Met. Eng. **39,** 230 (1932).) If both pair of *successive* isotopic forms of methylene chloride boil $y°$ apart; $\alpha = 1 + 0.035y$ for either pair. The composition of chlorine, Cl_2, is 57.6 per cent $Cl_2{}^{35-35}$, 36.6 per cent $Cl_2{}^{35-37}$ and 5.8 per cent $Cl_2{}^{37-37}$. (Giauque and Overstreet: J. Am. Chem. Soc. **54,** 1737 (1932).) Assuming the same ratios for the three isotopic forms of methylene chloride, and assuming their molal volumes in the liquid state to be identical, one calculates $1.32040-0.016y$ for limiting specific gravity of distillate. Comparing this with experimental values above given, it is seen that y must be 0.005°C. or less. This result is apparently at variance with the claim (Keesom and van Dijk: Proc. Acad. Sci. Amsterdam **34,** 42 (1931)) of a recognizable separation of the isotopes of neon in a reversible distilling column of nineteen actual plates.

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[1] Aided by grants from the Committee for Research in Problems of Sex of the National Research Council, and from the Rockefeller Foundation. These funds have been generously augmented by the Board of Research and the College of Agriculture of the University of California.

The 6.09 meter column will separate in better than 95 per cent purity (with a single distillation), liquids boiling as little as 5°C. apart. The time for maximum enrichment at total reflux is then about twenty-four hours (one day). Hence even with a difference of 0.005°C. (the maximum possible for methylene chloride isotopes), to get about 95 per cent purity of isotopes, such a column must be 6 × 1000 or 6000 meters high, and the time for maximum enrichment would be increased to 1000^2 or 10^6 days. However, the right set of conditions for such a fractionation may have occurred in some places during the formation of the earth.

SUMMARY

The boiling points of successive isotopic forms of methylene chloride (due to the chlorine 35 and 37) are shown experimentally to differ by 0.005°C. or less. Hence in a liquid-vapor equilibrium type of fractionating column, the necessary height and particularly the necessary time of distillation, eliminate this method of separation. However this kind of fractionation may have occurred naturally in suitable geological formations.

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CORRECTIONS

The following corrections should be made in the article "Application of the Double Layer Theory of Otto Stern. I.", appearing in This Journal **36**, 3157 (1932):

In equations 6 and 7, read a + sign instead of the − sign.
In equation 8, read "$\mathfrak{Z} = 4 \times 1.67 \times 10^{2}$ "
In equation 9, read "295" in the exponent of e, instead of "2.95."
In equation 15, the exponent of e should read:

$$\begin{array}{c} 9\ 65 \times 10^{4} \times 3 \times 10^{9} \times 0\ 124 \\ 3 \times 10^{2} \times 2 \times 1.99 \times 4.183 \times 10^{7} \times 295 \end{array}$$

In equation 17, read "2.27×10^{-19}," instead of "$2\ 27 \times 10^{-17}$."

Frank Urban.
H L. White.

NEW BOOKS

Our Mineral Civilization. By THOMAS T. READ. Century of Progress Series. 5 x 7 in.; 165 pp. Baltimore: The Williams & Wilkins Co., 1933. Price: $1.00.

The author is a well-known writer in the field of mining engineering. The treatise on this subject is exceptionally well written and should be especially interesting to people who have not been trained as scientists and engineers.

The development and uses of the commercial minerals, important chemical elements, metals, and their alloys as applied by mankind is presented by the author in an interesting, clear, accurate, and concise manner. There are statistics, but not enough to bore the reader, and the general philosophy, economy, and comparisons remind one, to some extent, of the book *Creative Chemistry* by the late Dr. E. E. Slosson.

R. L. DOWDELL.

Säure-Basen-Indicatoren. Ihre Anwendung bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration. VON I. M. KOLTHOFF unter Mitwirkung von HARRY FISCHGOLD. 13.5 x 20.5 cm.; xi + 416 pp.; 26 figures. Berlin: Julius Springer, 1932. Price: 19.8 RM (geb.).

This volume, issued under a different title, is a much expanded fourth edition of *Der Gebrauch von Farbindicatoren.* The work is divided into three parts. The first two sections, i.e., "The dissociation of strong and weak electrolytes" and "The properties of acid-base indicators" contain an excellent discussion of the theory and modern viewpoint of these subjects. The third section dealing with "The colorimetric estimation of hydrogen ion concentration" contains the applications of the theories which have been developed to problems of practical application.

Probably no one is better qualified to write a handbook such as this than is Dr. Kolthoff, for it represents a field to which he has given major attention for a number of years, both as a research worker and as a teacher. The theoretical discussions go beyond most books which are designed to cover this field and include lucid discussions of the recent trends in the "activity" concept, including a thorough discussion of Brönsted's ideas on acid-base function. Brönsted has rightly pointed out that the hydrogen-ion, being a naked proton and accordingly an α particle, cannot exist as such except for an infinitesimally small length of time, that it will penetrate into the electron shell of the first molecule it comes in contact with and, thus associating itself with a neutral molecule, will form a molecule possessing a positive charge. Thus instead of speaking of "hydrogen-ions" we should more properly speak of the "hydronium ion concentration," (H_3O^+), which represents the concentration of the solvated protons. The Brönsted definition of acids and bases differs considerably from the older conceptions, but appears to possess real merit. Thus "an acid is a substance which is able to split off a proton, simultaneously forming a base, and a base is a substance capable of uniting with a proton, thus forming an acid." Thus the dissociation of an acid in water may be written

$$\underset{\text{acid}}{A} + \underset{\text{base}}{H_2O} \rightleftarrows \underset{\text{base}}{B^-} + \underset{\text{acid}}{H_3O^+}$$

This concept lays primary emphasis on the sign and magnitude of the charge of the central atom of a molecular configuration as determining acidic or basic properties rather than the criterion of "salt formation" which is regarded as an incidental phenomenon.

The present volume is especially valuable since it discusses acid-base dissociation in such solvents as ethyl alcohol. On the basis of Brönsted's definition both ethyl alcohol and water are bases, but water is four hundred times as strong a base as is ethyl alcohol; this accounts for the difference in behavior between aqueous and alcoholic systems. This section of the book especially appealed to the reviewer.

In the section devoted to the properties of indicators we find an excellent theoretical discussion, followed by a description of the various indicators, including formulas, melting point, and other physical properties, methods of purification, solubility and pH range and their suitability for use under various conditions and with various solvents. A new definition of an indicator is proposed, i.e. "Indicators are (apparently) weak acids or bases, whose inogene or aci- (or baso-) form possesses a different color and structure than the pseudo or normal form."

The third section of the book, dealing with the colorimetric estimation of hydrogen-ion concentrations, deals with the preparation and properties of buffer solutions, the technic of the colorimetric determination of hydrogen-ion concentration, the sources of error in the colorimetric methods, including an extended discussion of the effect of salts, proteins, and other colloids, temperature, etc., with the last chapter devoted to indicator papers. The book closes with an appendix of six tables showing the ion product of water at various temperatures, the ion activity product of water, the activity coefficient for various concentrations of electrolyte solutions, an extensive table of the dissociation constants of approximately one hundred and twenty acids and bases, including such compounds as the alkaloids, phenols, etc. (The reviewer wonders why the amino acids were omitted from such an imposing list, for they certainly are more commonly worked with than are many compounds included in the table), and an interpolation table for converting fractions of pH into C_H values. Excellent author and subject indices close the volume.

It is a book filled with valuable discussion and tabular data. The fact that other volumes on the determination of hydrogen-ion concentration are available should not deter one from purchasing this book, for it contains much material not otherwise readily accessible. It should be in every chemical library and in the hands of everyone interested in the control and measurement of hydrogen-ion concentration.

ROSS AIKEN GORTNER.

Die Struktur der Atomkerne. By DR. SIEGMUND STRANSKY. 22 x 15 cm.; 50 pp. Leipzig u. Wien: F. Deuticke, 1932. Price, 4s. 9*d*.

Dr. Stransky's monograph on the structure of the nucleus is entirely original and entirely speculative. There is evidence in favor of the conclusions he draws but it is of a numerical kind, in which the numbers are confined rigorously to integers. He does not consider other theories of the subject he is writing about, and it is at once patent to a reader that little reconciliation is possible between Dr. Stransky's views and the main *corpus* of knowledge that has been ground out of the research of the past twenty years. They lie, indeed, so far outside of the main stream of theory and experiment that I fear atomic physicists may fail to give them the patient consideration the author would like them to get.

Dr. Stransky is a modern Prout, a Prout, moreover, who has had in his time the discouragement of a Newlands. He tells us that for forty-five years he has occupied himself at invervals in arranging units of mass (protons, they would now be called) in such patterns that the most likely of them sum to the masses of the common elements, and that he has not always been able to get his work published. Like Prout he has started from the assumption that protons are the stuff from which all matter is built. The new points are that the protons are probably arranged in the nucleus in hexagons or fused hexagons like the CH groups in benzene, naphthalene, phenanthrene, and so forth, and secondly that the masses of the atoms of the elements of one particular group are based on one another. (For this purpose the subdivisions A and B of the groups of the Periodic Classification are ignored.) The atomic weights of copper and silver, for example, are based on those of lithium and the alkali metals. Just as naphthalene may be regarded as two benzenes less four carbon atoms, and picene as five benzenes less eight carbon atoms, so are heavy elements of a group so many times the masses of simple elements of the group less so many hydrogens. Thus Na, 23, is 4Li − 5, the atomic weight of lithium being taken exactly as 7, and Cs, 133, is 6Na − 5; the reason for subtracting 5 in these cases is that when four or six "benzene-rings" of protons are joined together most compactly there are five points held in common, and consequently no protons there. Occasionally some latitude is allowed in deciding what arrangements are most compact, and the various alternative masses arrived at serve as the various isotopes of the element under consideration. Thus nine "bricks" of twenty-three protons can be simply arranged so as to have either eight or ten points of contact with the possibility that the element so built up can have two alternative masses differing by two units. Much of the book is occupied with diagrams showing the patterns in which the nuclei of the atoms of the different elements are arranged by Dr. Stransky. The simpler ones look like the diagrams of carbocyclic chemistry; the more complex resemble snow crystals viewed through a microscope.

Dr. Stransky's general theory may have been plausible in days when atomic weights were thought to be whole numbers, or even in the early days of nuclear theory when the nucleus was regarded as built up of hydrogen protons, but the experimental work of F. W. Aston completely disposes of Prout's hypothesis in any form. It is the helium nucleus which is the chiefest brick in the nucleus, with the proton and possibly the neutron and the "demi-helion" as subsidiaries. None of these is any sort of arrangement such as Dr. Stransky postulates. The great importance of these ultimate units and the nuclei which are built from them at the present time is not that their masses are 4, 1, 2, 133, etc., but that their masses are in excess or defect of integers to an amount which is a function of their closeness of arrangement in the nucleus. Further, Aston has shown that there is little evidence of what might be called a periodic arrangement of the nucleus akin to that of the planetary electrons in an atom; if there were, one might deduce from the masses of the isotopes of tin those of the isotopes of lead by adding a constant amount, such as 88, to the masses of tin. To some degree this works, but it is not so universally applicable as to be regarded as an arrangement.

If further considerations were needed to be quoted against Dr. Stransky's theory, the experimental work on the discription of the nucleus which has been going on at Cambridge since 1919 would suffice. What is known of the nucleus from these experiments (and it is almost everything that is known) has no resemblance to Dr. Stransky's speculations.

Nevertheless Dr. Stransky has shown great ingenuity in his work. It is quite the best exposition of 'Proutism' that has appeared, and if it encourages others to begin a study of how the nucleus is built up from the real ultimate units, his labor will not have been altogether in vain.

A. S. Russell.

Chemische Technologie der Neuzeit. By O. Dammer. Second and larger edition, 5th volume. 19.5 x 27.5 cm.; xvi + 876 pp. Stuttgart: Ferdinand Enke, 1932. Price, bound RM.79, unbound RM.5.

This work deals with metals and alloys, and is one of those typical monuments of German industry and scholarship which not only demand but compel admiration. It begins with a good account of the technical methods of the preparation of alloys, and a comprehensive account of a formal phase rule treatment.

The book is full of excellent photographs; the colored ones are especially noteworthy.

From the point of view of the practical man the book is of the greatest interest. There are excellent photographs, for example, in the section on brass, of the serious technical defects which arise through the use of wrong temperatures. The references to the literature are numerous, and the reviewer, who has checked about twenty, has found them all correct.

It is difficult to see how anybody interested in non-ferrous alloys can afford to be without this book.

F. A. Freeth.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut fur Silikatforschung in Berlin-Dahlem. Edited by Wilhelm Eitel. 29 x 21 cm.; 212 pp. Brunswick: Friedr. Vieweg und Sohn, 1932. Price RM.28.

The proceedings of this active Institute again cover a wide range. Working as it does in close coöperation with the silicate industries, it has been found necessary to widen the scope to include the study of the heat balance in technical processes, such as the manufacture of Portland cement. In this connection a description is given of the new 'Lepol' kiln, which although of German design has so far been erected only in Spain and in Luxembourg. By the use of a preliminary roasting chamber utilizing the waste heat, the actual kiln is greatly shortened, and a very considerable economy of fuel is effected. Other work on cement includes a study of the setting time of mixtures of Portland and aluminous cement, from which it appears that the properties of the mixtures are not additive.

Glass problems fill the greater part of the volume. With the help of the German glass manufacturers, a set of tables of the properties of glass, taking into account some 2500 publications, is in course of preparation. These tables will include the chemical as well as the physical properties. Several communications deal with the removal of color from glass, especially by means of cerium. Cerium dioxide is superior for this purpose to manganese dioxide, but it will cause darkening by ultraviolet light if arsenic or bismuth be present. This effect is corrected by the addition of small quantities of sodium sulfate, and the mutual influence of these additions is worked out. In opal glass, the crystals producing turbidity are identified as cristobalite, whatever the composition of the glass, although in fluoride glasses the presence of minute crystals of sodium fluoride has also been proved. The hydrothermal synthesis of calcium silicates and the action of carbonic acid under high pressure on the silicates have been studied, one result being the preparation of definite carbonate-silicate glasses, containing as much as 20 per cent of sodium carbonate. This memoir includes an interesting series of quantitative experiments on the equilibrium between carbon dioxide and glasses. The flow of molten glass in the Owens machine is considered theoretically, this paper to be followed by one in which the theoretical deductions are to be tested by an examination of the flow lines as shown by Schlieren.

As in previous years, there are several descriptions of improved apparatus and experimental methods, and a few communications having only an indirect bearing on the silicate industries are included, such as a study of vanadium oxide sols and another in which the dehydration and rehydration of brucite is examined, it being shown that a new phase is formed, and not simply a pseudo-structure. The editor is to be congratulated on the quality of the work done under his direction, and on the excellent presentation of it in this handsome volume.

C. H. Desch.

THE SOLUBILITY OF SILVER IN MERCURY. II

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Determinations of the solubility of silver in mercury at various isolated temperatures have been reported by several investigators (5, 8, 17, 14, 12, 15, 24), but Joyner (9) was the first to study the problem systematically. Several years ago Sunier and Hess (22) published some precise work on the solubility of silver in mercury over the range 80°C. to 200°C. Their results agreed remarkably well with those obtained by Joyner, who used a rather crude method. Since that time Murphy (13) has published a complete phase diagram for the system silver–mercury. He was interested, however, in the composition of the solid phase and cites the data of Sunier and Hess (22) for his liquidus curve at low temperatures.

Since Joyner (9) is the only person offering systematic data below 80°C., (four determinations) and his data in this range of temperature pointed to a marked flattening out of the solubility curve below 50°C., it was thought advisable to extend the precise work of Sunier and Hess (22) below 80°C.

MATERIALS

The mercury used was first purified by dropping it through a five-foot Meyer column containing 6 *N* nitric acid and was then washed with distilled water. The dried mercury was distilled in an all glass apparatus according to the method of Hulett and Minchin (7). Samples of this mercury yielded no weighable residue when evaporated according to the method of analysis of the amalgams in a stream of hydrogen.

The silver used was "1000 fine" foil, kindly supplied by the Philadelphia Mint. This foil was used as the solid phase either directly or after treatment by methods described later in this paper

APPARATUS

The solubility tube used, a modification of the one used by Sunier and Hess (22) and similar to the tube used by Sunier and Gramkee (21), was made of Pyrex glass. It differed in size from that of the latter, as the smaller solubility necessitated the employment of larger volumes of mercury.

The shaking mechanism differs little from that used by Sunier and White (23) with the exception that in one run a set of sixteen rather than eight tubes were run at the same time. The apparatus brought about complete transfer of the contents of the tube from one end to the other by rotating it through an angle of sixty degrees.

The tubes were immersed in a heavily lagged thermostat similar to the one described by Sunier and White (23). The bath was heated by electricity and steam, and was provided with a copper cooling coil. In the early runs, manual control of the temperature was resorted to, but in later runs a mercury thermoregulator of the type described by Clark (1) was used. When manual control was used the constancy approached ±0.02°C., while with the thermoregulator the temperature was held within the range of ±0.01°C.

Temperatures were read from mercury thermometers of the double diamond label manufactured by Hiergesell Brothers, and graduated in tenths of a degree. These thermometers were compared with thermometers standardized by the Bureau of Standards. The ice points were taken frequently but showed no change. Temperatures could be read to 0.02°C. with ease. Changes of temperature during the run were noted from a Beckmann thermometer inserted in the bath.

The weights used were calibrated according to the method of Richards as described by Fales (4) and compared with a weight checked by the Bureau of Standards.

EXPERIMENTAL PROCEDURE

After the solubility tube had been washed with 6 *N* nitric acid and distilled water, it was dried in an oven at 160°C. overnight or flamed with a Bunsen burner in a stream of air. The tube was then charged with 135 to 155 g. of mercury in the manner described by Sunier and Gramkee (2) and two to three hundred per cent excess of the silver required at that temperature, using Joyner's (9) data as a guide. The tubes were flamed and evacuated with a Cenco Hyvac pump to a pressure of 0.01 to 0.1 mm. of mercury read on a MacLeod gauge.

To determine the solubility at a certain temperature a total of eight tubes was made up (16 tubes in Run N). The run was made in the manner described by Sunier and White (23), four tubes being rotated at 5°C. above the solubility temperature preliminary to the insertion of the remaining tubes.

Later in the research it became evident that equilibrium had not been attained in the time allowed, so that all of the tubes were inserted at the same temperature and rotated for periods of from eight to two hundred and fifty-six hours.

Sampling was carried out in the manner described by Sunier and White (23).

The method of analysis was that used by Sunier and Gramkee (21) in the analysis of gold amalgams. A large Pyrex tube with a ground glass stopper, as shown in figure 1, was supported in an electric furnace. A mercury trap was provided to catch the condensed mercury swept through by the gas admitted at the opposite end. The capsules were supported on Sillimanite slabs, hence there was no possible contamination of evaporated mercury.

In order to test the applicability of this procedure to silver amalgams, various experiments were carried out. It was found that the mercury used left no weighable residue when evaporated by this procedure. Weighed pieces of silver foil lost no weight when heated for periods of twenty hours at 550°C. in a stream of hydrogen. Mercury was placed on this foil and then driven off by heating at 270°C. to 300°C.; the residues were then heated to 550°C. for several hours. When air was used the residues were consistently several tenths of a milligram heavier than their original weight. This could not be due to silver oxide formed, for it would be unstable at the temperatures employed, according to the free energy relationships cited by Lewis and Randall (11). Owing to the finely divided condition of the crystallized silver, occlusion suggests itself as a possibility. Steachie (20) refers to the occlusion of gases on finely divided metallic surfaces. When hydrogen, purified by bubbling through saturated solutions of potassium permanganate, sodium hydroxide, and 95 per cent sulfuric acid was used the residues came down to their original weight.

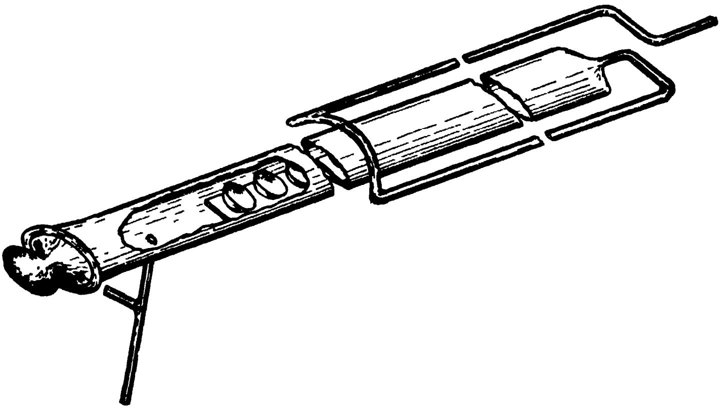

FIG. 1. EVAPORATION TUBE

To test the entire experimental procedure, eight tubes containing weighed quantities of silver and mercury were made up and carried through the entire procedure. The results of this experiment are tabulated in table 1. It is to be noted that the solubility of silver is much less than that of gold, so that, of necessity, much smaller residues must be weighed, and the amounts of mercury used must be much larger. Despite these disadvantages, from the composition found, the average deviation was less than one part per thousand.

TABLE 1

TUBE	SILVER TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION
	grams	*grams*			*parts per thousand*
1	0 0912	143 928	0 1177	0 1182	4 2
2	0 0986	147 909	0 1238	0 1228	8 1
3	0 0877	145 417	0 1120	0 1124	3 5
4	0 0859	143 349	0 1113	0 1122	8.1
5	0 0949	144 816	0 1217	0 1218	0 8
6	0 0899	145 311	0 1148	0 1142	5 3
7	0 0940	137 088	0 1273	0 1267	3 9
8	0 0930	145 897	0 1184	0 1179	4 2
Average =			0 1184	0 1183	4 8

Deviation of average composition = 0 85 per 1000

TABLE 2

Run A

Time of run 6 hours (low side–4 hours); temperature 40.11°C (high side–45.3°C.); silver—foil (mint); mercury—triple distilled.

TUBE NUMBER	SILVER AT START	WEIGHT OF AMALGAM	WEIGHT OF SILVER	ATOMIC PER PER CENT OF SILVER	DEVIATION FROM MEAN	REMARKS
		grams	*grams*		*p p t*	
A-1	0 5	142 991	0 0880	0 1144	5	
A-2	0 5	144 533	0 0886	0 1139	0	
A-3	0 5	143 692	0 0872	0 1128	11	
A-4	0 5	142 416	0 0932	0 1216	x	Exclude
A-5*	0 5	146 070	0 0896	0 1140	1	
A-6*	0 5	142 993	0 0880	0 1150	11	
A-7*	0 5	143 285	0 0879	0 1140	1	
A-8*	0 5	142 772	0 0867	0 1129	10	
		Average = Low side, 0 1137 High side, 0 1140		(3) 0 1139	5 per 1000	

Number of determinations, 7.

* High side.

EXPERIMENTAL RESULTS

In table 2 will be found a sample table of data for one run.

In table 3 will be found the table of data for Run N in which sixteen tubes were used and the solid phase varied as described later in this article.

TABLE 3

Run N

Time of run 256 hours; temperature 25.28°C.; silver as noted; mercury—triple distilled.*

TUBE NUMBER	SOLID PHASE	WEIGHT OF SOLID PHASE	WEIGHT OF AMALGAM	WEIGHT OF SILVER	ATOMIC PER CENT OF SILVER	DEVIATION FROM MEAN	REMARKS
		grams	*grams*	*grams*		*p p t*	
A-1	Reed	1 7	144 951	0 0606	0 0777	11	
A-2	Reed	1 6	143 811	0 0620	0 0801	35	
A-3	Reed	1 6	146 676	0 0685	0 0868	102	Exclude
Ex.	Foil	1 0	155 377	0 4891	0 5841	x	No glass wool
E-1	Ag_3Hg_4	2 0	140 474	0 0631	0 0835	69	Exclude
E-4	Ag	1 0	138 439	0 3189	0 4275	x	Filtered through chamois
E-2	Ag_3Hg_4	2 0	141 603	0 0570	0 0748	18	Exclude
E-3	Ag	1 0	134 842	0 0673	0 0928	162	Exclude
C-1	Ag_3Hg_4	2 0	143 694	0 0695	0 0899	133	
C-2	Ag_3Hg_4	2 0	141 549	0 0570	0 0749	17	No glass wool Poor vacuum
C-3	Ag_3Hg_4	2 0	85 435	0 0346	0 0748	18	
C-4	Ag_3Hg_4	2 0	148 444	0 0602	0 0754	13	
H-1	Ag	1 0	143 853	0 0703	0 0908	142	Exclude
H-2	Ag	1 0	143 467	0 0617	0 0799	33	
H-3	Ag	1 0	144 120	0 0593	0 0765	1	
H-4	Ag	1 0	144 399	0 0588	0 0757	9	
Average =					0 0766	21 1 per 1000	

Number of determinations, 9.

* With the exception of the tube marked Ex , column 1.

TABLE 4

RUN	TEMPERATURE	SOLUBILITY	DEVIATION	NUMBER OF TUBES	TIME
	degrees C		*parts per thousand*		*hours*
A	40 11	0 1139	5	7	6
B	50 02	0 1450	4	6	7
C	60 26	0 1901	27	8	7
D	70 54	0 2404	32	8	7
E	30 15	0 0965	91	8	7 Definite trend
F	80 94	0 2892	4	6	7
H	19 01*	0 0636	6	8	8
I	29 93*	0 0881	13	5	9
J	8 92*	0 0641	64	6	9
K	25 60*	0 0792	14	6	78
L	18 17*	0 0643	10	5	75
N	25 28*	0 0766	21	9	256

[1] All tubes approached saturation from the same side.

In table 4 will be found the summary of all runs.

Figure 2 is a plot of the log of the solubility versus the reciprocal of the absolute temperature. The slope of the line was determined from a large scale plot and the line corresponds to the equation

$$\log N = \frac{-1105\ 8}{T} + 0\ 5894$$

Of a total of one hundred and twenty-eight determinations made, thirty-eight have been rejected. Of this apparently large number of rejected

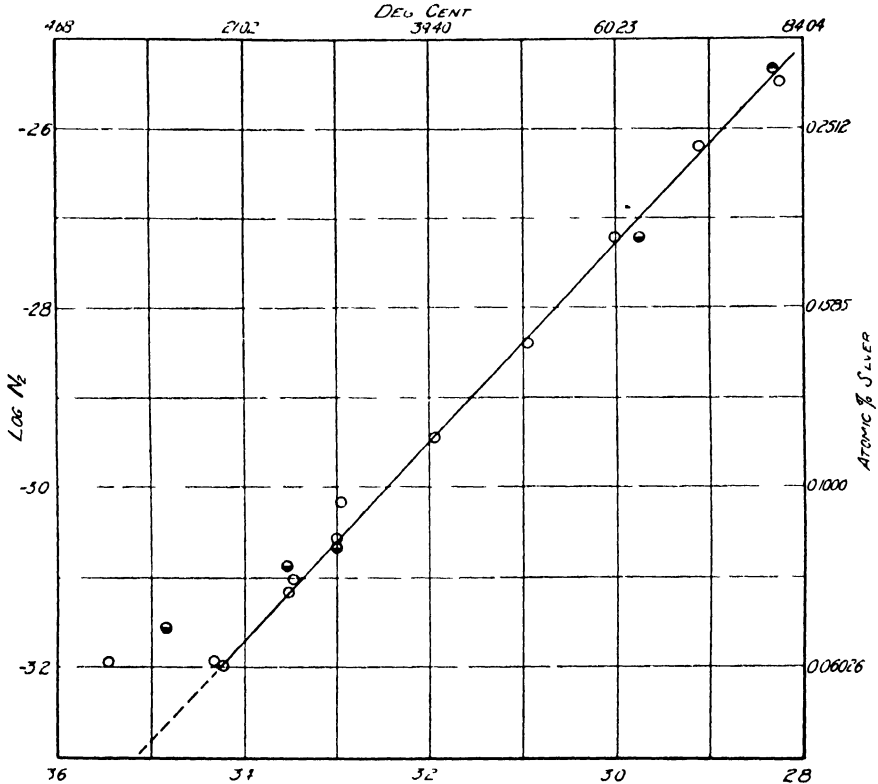

FIG. 2. THE SOLUBILITY OF SILVER IN MERCURY

⊖ Joyner; ● Sunier and Hess; ○ DeRight.

tubes, sixteen are accounted for by Runs G and M, where equilibrium was not attained. Of the remaining twenty-two excluded, four tubes were broken, three amalgams bumped during evaporation, and difficulty was experienced in the filtration of four tubes. Therefore only eleven tubes were excluded, merely because their deviation was greater than four times the average deviation.

DISCUSSION OF RESULTS

It was realized at the inception of this investigation that, owing to the slight solubility of silver, it would be necessary to employ large tubes and to weigh the residues extremely accurately. After the completion of the blank run and the satisfactory results obtained, it was felt that little further difficulty would be experienced.

The solubilities at temperatures above 40°C. were first determined. Although in some cases rather large average deviations were found, the determinations seemed to be in fair agreement, and when plotted fell on a straight line. The slope of this curve was somewhat less than that determined by Sunier and Hess (22). This change in slope is not unusual at lower temperatures. The determination at 80°C., which was the lowest temperature at which Sunier and Hess (22) made measurements, was in good agreement with their result. Furthermore, in the range of temperature above 40°C., the data was in agreement with that of Joyner (9).

A hint of the difficulty present in the behavior of amalgams below 40°C. was given by Joyner's data. There was a marked break in the slope of his curve at 40°C. The slope of the curve at the lower temperatures approached zero.

In Run E at 30.12°C. there was a marked discrepancy between the four tubes of the high side and those of the low side. This seemed to be a criterion that equilibrium had not been attained. A very marked discrepancy existed between the two sides in Run G at 19.85°C. This disagreement was so marked that this run was omitted from table 4.

It was decided to make a second run near the temperature of Run G, rotating all eight tubes, from the low side, for eight hours (Run H) at a temperature of 19.01°C. This run yielded very satisfactory results, since all eight tubes gave an average deviation of only 6 p.p.t., a very low figure for such a small solubility. Furthermore the point, when plotted, showed no deviation from the straight line drawn in figure 2.

Run E was repeated in the same manner in Run I. Unfortunately, two of the tubes were broken and a third excluded. The remaining five were in good agreement.

Run J yielded a curious result. It was carried out in the same manner as Runs H and I. Although the six determinations retained were not in good agreement, their average deviation of 64 per thousand pointed to some regularity. The apparent solubility was greater than that obtained at 20°C. and showed some agreement with Joyner's results.

The impression gained from a first reading of Joyner's paper was that he had rotated his tubes in a constant temperature bath for periods of a fortnight. Upon closer inspection of his paper it was found that he had rotated his amalgams containing *both* silver and tin for the time indicated, but he made no specific statement of the time of rotation in the silver–

mercury system. Furthermore, he claims the solubility he obtained was the equilibrium of Ag_3Hg_4 in contact with mercury, rather than of silver in contact with mercury. Murphy (13) states that silver amalgams attain equilibrium several times faster at 100°C. than at room temperature. Data is also available as to the rate of penetration of mercury into a silver surface at different temperatures (8). Therefore it seemed advisable to continue the runs at lower temperatures for longer periods of time.

Run K was to continue for seventy-five hours to note any difference in the solubility obtained at 25°C. Likewise new mercury was used in two tubes to see if any error could creep in, owing to the use of mercury evaporated from previous runs. The results of this run were in fair agreement among themselves and the mean result fell very close to the straight line obtained at higher temperatures.

Run L was a determination of the same type, at 18°C. Unfortunately, the contents of one capsule bumped, silver being transferred to two other capsules, so that it was necessary to exclude three values. The mean solubility obtained in this run was not in disagreement with previous runs, and fell on the straight line. This proved that the runs at 20°C. and 30°C. for a shorter period of time had practically reached equilibrium.

Run M was to continue for one week in the hope that equilibrium at 10°C. might be attained. This temperature was made possible through the use of a thermoregulator, cooling being brought about by pumping water from an auxiliary thermostat containing ice, through the copper cooling coil. In four of the tubes the solid phase consisted of silver which had been completely dissolved in mercury at a high temperature and then allowed to cool. The results of this run were very disappointing. There was too little agreement among the tubes to accord any credence to this determination. The four tubes, containing the solid phase mentioned above, filtered with great difficulty, the solid caking at the mouth of the capillary. Furthermore, the results showed a higher solubility than the other four, supporting the conviction that solid passed through with the liquid phase. Owing to the disagreement among the tubes this run was omitted from table 4.

At this point in the research a critical survey was made of the fourteen previous runs, with a view toward detecting any errors in procedure and introducing any helpful innovation. The following changes in procedure suggested themselves: (1) variation of the form of the solid phase, (2) variation of the liquid phase, (3) design of the tubes, i.e., the method of filtering, (4) the time of shaking, (5) the number of tubes.

Murphy (13), in his paper, states that equilibrium is much more readily reached when finely divided silver is used. Furthermore, it is to be noted that in the runs of Sunier and Hess (22) in which they obtained their smallest average deviation, silver filings rather than foil was used. Joyner claims his data to be that of Ag_3Hg_4 in equilibrium with mercury, and Murphy postulates the formation of this compound from the liquid phase at a higher temperature. It was decided to make use of this solid phase to explain the behavior of the amalgams.

The design of the tube would be rather dependent on the type of solid phase used. The use of glass wool above the capillary filter, or filtration through sintered glass, suggested themselves. A method of double filtration or decantation was considered, but did not appear to be applicable as finely divided silver, when wet with mercury, seemed to be dispersed quite uniformly throughout the liquid phase. The use of glass wool above a very fine capillary was deemed the most logical procedure.

An identical tube support was made so that sixteen tubes might be run at the same time.

The supplementary Run N was then made. A temperature of 25°C. was chosen because it could be easily attained and would establish the validity of the data to 20°C. The tubes used were identical with those previously used, with the addition of glass wool above the capillary. Although no objection to the use of the evaporated mercury could be found, it was decided to use new mercury. The time of shaking was increased to two hundred and fifty hours and sixteen tubes were used. Three distinct solid phases were used.

(1) Mr. G. H. Reed,[1] working in this laboratory several years ago on the solubility of silver in mercury at higher temperatures, made up several tubes containing silver and mercury. One of these tubes had been carefully preserved, but for some reason had not been analyzed. The silver had been in contact with the mercury for several years at room temperature. When opened, the solid phase was granular and brittle and retained none of the characteristics of the original foil. When all of the excess mercury was squeezed from the solid through a chamois, and a portion analyzed, it was found to have a composition approximating Ag_3Hg_4.

(2) Since Murphy cites the formation of Ag_3Hg_4, it was decided to attempt to prepare this compound. Weighed amounts of silver and mercury in the proportion of Ag_3Hg_4 were sealed in a tube and evacuated; the tube was so constructed that, by inversion, the contents could be transferred from one end to the other through a capillary. This acted as a criterion when the contents were entirely liquid. This tube was heated at 250°C. for forty hours, then raised to 500°C. and the contents filtered three times at intervals of one hour, thus insuring homogeneity of the contents. The tube was then cooled to 300°C. and held for twenty-four hours, cooled to 250°C. and held for fifty hours, and kept in an oven at 100°C. until introduced into the tubes. The contents of the tube were entirely solid, and had a bright crystalline appearance.

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[1] See footnote (a), Sunier and Hess (22).

(3) Finely divided silver was prepared in a manner similar to that described by Tartar and Turinsky (25), who refer to Lewis (10). Some modifications were made. The silver employed was the "1000 fine" foil, and C. P. chemicals were used. The silver carbonate was heated in a stream of hydrogen at 250°C. to 300°C. for six hours, and then raised to 500°C. until there was no further loss in weight.

The temperature throughout the run was very constant, the thermoregulator being used. Two tubes were broken at the inception of the run. The contents of one was transferred to a tube with no glass wool, but yielded a very high result. The contents of one tube refused to filter, so they were removed and quickly squeezed through a chamois skin. The very high silver content obtained in this case is of significance.

The average solubility obtained from this run agreed very well with the straight line plot, hence establishing the straight line function to 25°C. or lower. Furthermore, the different variables used seemed to clear up any question of variable phases employed.

A consideration of available data leads one to some interesting speculations. First of all, the term "solubility" must be defined. Richardson (18) states, "a solution is a body of homogeneous character, the composition of which may be varied continuously within certain limits." Lewis and Randall (11a) give a more fundamental definition. Definitions may vary but the idea of homogeneity is always retained. Next the criterion of homogeneity must be defined. In ordinary aqueous or organic systems, this idea is overlooked, for the appearance of the solution is an immediate criterion. A cloudy or translucent appearance postulates a colloid sol, while a clear appearance is evidence of a real solution. The effect of light, then, is the means of classification in these systems. In the mercury system, the opacity prevents determination of the clearness, so that the amount of material that passes through the filter in the liquid phase has been a criterion of solubility. Too little attention has been paid to the size of the filter or conditions of filtration, i.e., pressure.

It is this fact that may account for the many discrepancies in data reported. Russell (19), working on amalgams other than silver and gold, reports some interesting findings. His method of analysis relies on the preferential oxidation of metals less noble than mercury, by shaking the amalgam with a solution of potassium permanganate. In one study he filtered identical amalgams through a Jena glass sintered filter and through chamois skin. He found the use of the chamois skin very unreliable, the apparent solubility inconstant and several times larger than when filtered through the sintered glass filter. This is in agreement with the result obtained when a chamois skin was used in Run N. A large majority of the excluded determinations in this paper have been "high."

Until there is some method of determining a homogeneous phase, other than filtration, the term "solubility" in a metallic system has a limited meaning, for particles may vary in size from atomic proportions to large aggregates. If this is true, and there is not a sharp gradation, solubility will be dependent on the conditions of filtration. Apparently, in the silver–mercury system, there is a distinct difference in size of silver particles above 40°C., while below that temperature there seems to be a gradual gradation. It seems, therefore, that the greatest credence should be accorded to the lowest results, provided that enough time has elapsed for equilibrium to be reached.

There is a possibility that a measurement of the light reflected from an amalgam, or some other optical means may be used by which homogeneity may be determined.

SUMMARY

1. Amalgams as dilute as 0.06 atomic per cent have been prepared, and analyzed with a precision approaching one part per thousand.

2. One hundred and twenty-eight determinations of the solubility of silver in mercury in the range 20°C. to 80°C. have been made.

3. Several forms of silver and intermetallic compounds have been used as the solid phase.

4. In the range of temperature from 20°C. to 80°C. the solubility changes according to the equation

$$\log N = \frac{-1105\ 8}{T} + 0\ 5894$$

5. The relation of the term "solubility" to particle size has been briefly discussed.

In conclusion the writer wishes to express his sincere appreciation to Professor Arthur A. Sunier who has so inspiringly and unselfishly directed this research.

REFERENCES

(1) Clark: Determination of Hydrogen Ions. The Williams & Wilkins Company, Baltimore (1917).
(2) de Souza: Ber. **8**, 1616 (1875); **9**, 1050 (1876).
(3) Eastman and Hildebrand: J. Am. Chem. Soc. **36**, 2020 (1914).
(4) Fales: Inorganic Quantitative Analysis, paragraph 82, p. 103. The Century Co., New York (1925).
(5) Gouy: J. Physics **4**, 320 (1895).
(6) Harteck: Z. physik. Chem. **134**, 1 (1928).
(7) Hulett and Minchin: Phys. Rev. **21**, 388 (1905).
(8) Humphreys: J. Chem. Soc. **69**, 243 (1896).
(9) Joyner: J. Chem. Soc. **99**, 195 (1911).
(10) Lewis: J. Am. Chem. Soc. **28**, 158 (1906).

(11) Lewis and Randall: Thermodynamics, p. 480. McGraw-Hill Book Company, New York (1923).
(11a) Ibid. p. 10.
(12) Mayey: Z. Physik **50**, 209 (1905).
(13) Murphy: J. Inst. Metals, March, 1931.
(14) Ogg: Z. physik. Chem. **27**, 285 (1898).
(15) Parravano and Jovanovich: Gazz. chim. ital. **49**, 6 (1919).
(16) Piersal: Phys. Rev. **23**, 785 (1925).
(17) Reinders: Z. physik. Chem. **54**, 609 (1906).
(18) Richardson: General Chemistry. Henry Holt and Company, New York (1928).
(19) Russell: J. Chem. Soc. **32**, 835 (1932); **32**, 891 (1932).
(20) Steachie: J. Phys. Chem. **35**, 2113 (1931).
(21) Sunier and Gramkee: J. Am. Chem. Soc. **51**, 1703 (1929).
(22) Sunier and Hess: J. Am. Chem. Soc. **50**, 662 (1928).
(23) Sunier and White: J. Am. Chem. Soc. **52**, 1842 (1930).
(24) Tammann and Strassfurth: Z. anorg. Chem. **143**, 357 (1925).
(25) Tartar and Turinsky: J. Am. Chem. Soc. **54**, 580 (1932).
(26) Van Hetteren: Z. anorg. Chem. **42**, 128 (1904).

THE DETERMINATION OF THE ISOELECTRIC POINT

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The isoelectric point may be calculated as outlined by Kuhn (1) and Simms (2) from the basic and acidic ionization constants of the oxide. These constants are often unreliable. This electrometric method is suggested as a means of measuring the isoelectric point of an amphoteric oxide.

MATERIALS AND APPARATUS

A. Mercuric oxide. One of the best grades of commercial oxides, red variety, was used. Half-cells containing this commercial form of mercuric oxide gave potentials which agreed to within 0.0001 volt with half-cells containing red mercuric oxide prepared by decomposing purified mercuric nitrate.

B. Lead oxide, red variety, was precipitated from a hot 12 normal solution of potassium hydroxide, as described by Smith and Woods (3) by adding powdered lead acetate to the hot alkali. The oxide was washed by decantation with hot 10 normal potassium hydroxide, then washed thoroughly and repeatedly with hot distilled water, and dried over sulfuric acid in a vacuum desiccator. Analysis for lead, according to the gravimetric method of Brown, Moss, and Williams (4) gave 99.7 per cent of PbO. A small amount of water was evolved when the oxide was heated strongly.

C. Lead oxide, hydrated, was precipitated from a dilute lead acetate solution by the addition of a dilute solution of potassium hydroxide at room temperature. The precipitate was washed by decantation with warm distilled water and dried over sulfuric acid in a vacuum desiccator. Analysis gave the ratio of hydroxyl to lead as being very close to 2:1, showing the absence of a basic salt. The per cent of lead was 89.77, which agrees well with Mueller (5) who found 89.75 per cent and represented the composition of the oxide by the formula $(PbO)_3H_2O$, which requires 90.40 per cent of lead.

D. Potassium hydroxide solution was prepared as described by Ming Chow (6). A 50 per cent solution of one of the best grades of potassium hydroxide was electrolyzed in a tall form beaker, using a large sheet of platinum foil (8 × 10 cm.) for the anode and about 2 kilograms of redistilled mercury for the cathode. The beaker was covered and the mercury was stirred during electrolysis. A current of 10 to 15 amperes was passed through until the amalgam had become so crystalline it could no longer be stirred. It was washed several times with distilled water, then transferred to a 3-liter flask, and washed a few more times in the absence of carbon dioxide. The flask was then filled with distilled water and connected with a filtering tube and another flask. After about two weeks the amalgam had decomposed and the solution was filtered through an asbestos filter. The filtering tube was removed and a carbon dioxide trap, which permitted filling of a weight buret, was attached. The solution at no time gave a test for carbonate. The molality of the solution was determined by titrating with hydrochloric acid, standardized against sodium carbonate, and also by titrating against benzoic acid. Weight burets were used in these titrations. Solutions containing 0.1 mole of potassium hydroxide per thousand grams of water, were made up gravimetrically and the more dilute solutions made by diluting these, using calibrated pipets and volumetric flasks.

E. Doubly distilled water, distilled in an all Pyrex still, first from alkaline permanganate and then redistilled from the clean still, was used. It was kept in 5-gallon bottles and was protected from the carbon dioxide of the air.

Saturated solutions of the oxides were made in 200-ml. round bottomed, long necked flasks, fitted with ground glass stoppers and provided with rubber caps to prevent carbon dioxide from working past the ground glass stoppers. These flasks were almost filled with solvent, an excess of the solid oxide added, and then shaken in a constant temperature air bath at 25.0 ± 0.2°C.

Electrode vessels were kept in a thermostat bath at 25.00 ± 0.05°C.

Each half-cell consisted of a Pyrex test tube with a side arm, and a tube sealed on at the bottom and bent upward, carrying a smaller tube with a platinum wire sealed in at the lower end. It was stoppered with a rubber stopper coated with stopcock grease in order to prevent carbon dioxide from entering.

The side arms of the cells were dipped in a beaker containing the same solution that was in the cells, and covered with a layer of paraffin to prevent evaporation.

The only electrode vessel which presents enough novelty to warrant showing in a diagram, is the vessel shown in figure 1. This cell makes possible the measurement of potentials in very dilute solutions, even less than 0.0001 molal. The rate of diffusion in this vessel was tested with a dilute potassium permanganate solution. A number of days were required for the permanganate to diffuse from the right half into the left half of the cell.

All potentials were measured with a Leeds and Northrup type K potentiometer. The standard cell was checked frequently against a new cell, checked by the Bureau of Standards.

EXPERIMENTAL PART

The rate of solubility and nature of a solution of lead oxide, as given in the literature, is so uncertain that a few investigations were carried out in connection with this problem.

Randall and Spencer (7) determined the solubility of three lead oxides in alkaline solutions, ranging in concentration from about 0.05 to 0.3 molal. They claimed that in order to obtain saturated solutions of lead oxide, red variety, it was necessary to shake mixtures containing an excess of solid oxide for from twenty to fifty days. They shook the hydrated oxide, $(PbO)_3H_2O$, for from five to thirty days.

TABLE 1

Rate of solubility of $(PbO)_3H_2O$ *in water*

TIME OF STIRRING	MOLES OF Pb IN 1000 GRAMS OF SOLUTION
5 minutes	$5\ 50 \times 10^{-4}$
15 minutes	$5\ 75 \times 10^{-4}$
50 minutes	$5\ 78 \times 10^{-4}$
4 hours	$5\ 76 \times 10^{-4}$
24 hours	$5\ 72 \times 10^{-4}$

TABLE 2

Rate of solubility of PbO *(red) in approximately 0.1 molal* KOH *solution*

TIME OF STIRRING	MOLES OF Pb IN 1000 GRAMS OF SOLUTION
20 minutes	$3\ 897 \times 10^{-3}$
3 hours	$4\ 193 \times 10^{-3}$
7 hours	$4\ 356 \times 10^{-3}$
25 hours	$4\ 417 \times 10^{-3}$
48 hours	$4\ 429 \times 10^{-3}$
122 hours	$4\ 425 \times 10^{-3}$

We determined the rate of solubility of hydrated oxide in pure water, and the rate of solubility of red oxide in approximately 0.1 molal potassium hydroxide solution, by adding about 3 g. of the solid oxide to about 2 liters of the solvent contained in a 3-liter conical flask, fitted with a stirrer equipped with a vaseline seal to exclude carbon dioxide, a filter tube containing an asbestos filter, which permitted withdrawal of samples while the solution was being stirred, and an inlet tube connected with a source of carbon dioxide-free air. Stirring was just vigorous enough to keep the major portion of the solid oxide suspended in the solvent. Samples were withdrawn through the asbestos filter at various intervals from the time stirring was started and were analyzed for lead. The results of the measurements are given in tables 1 and 2.

From the above measurements it would appear that saturated solutions of the hydrated oxide can be obtained in a few hours, and saturated solutions of the red oxide in a few days. The hydrated oxide was shaken for at least twelve hours and the red oxide for from seven to ten days.

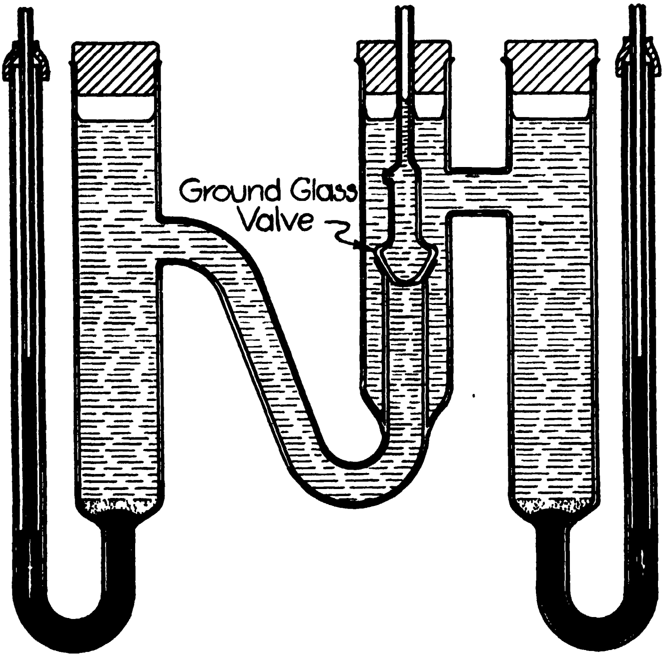

FIG. 1

In order to determine the basic characteristics of lead oxide and perhaps give a better idea of the nature of the solution, concentration cells of the type

$$Hg - HgO_{(s)} - KOH \parallel H_2O - PbO_{(s)} - HgO_{(s)} - Hg$$

were set up and measured in electrode vessels of the type shown in figure 1. The electrolyte in the right half-cell consisted of a saturated solution of lead oxide in water, while the electrolyte in the left half-cell consisted of potassium hydroxide solution.

The reaction in such a cell, when an electron current flows through the cell from right to left is

$$Hg + 2OH^- \rightarrow HgO + H_2O$$

in the left half-cell and

$$HgO + 2H_2O \rightarrow Hg + 2OH^-$$

in the right half-cell. The total change is the formation of OH^- in the right half-cell and consumption of OH^- in the left half-cell. The E of this cell must then depend upon the activity of the hydroxide ion in the two half-cells. The molality of the potassium hydroxide was varied and the E of the cell measured. When E is zero, the activity of the hydroxide ion in the two half-cells must be equal. This must be almost the same as the molality of the potassium hydroxide when the measured E is zero. Under these conditions the liquid junction potential will be very small.

TABLE 3

E.M.F. of cells $Hg - HgO_{(s)} - KOH \parallel H_2O - PbO_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE E OF CELL
0.0010	0.0450	0.0435	0.0443
0.0004	0.0260	0.0255	0.0257
0.0002	0.0003	0.0004	0.0004
0.0001	−0.0135	−0.0165	−0.0150

TABLE 4

E.M.F. of cells $Hg - HgO_{(s)} - KOH \parallel H_2O - (PbO)_3H_2O_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE E OF CELL
0.0010	0.0280	0.0190	0.0235
0.0004	0.0088	0.0090	0.0089
0.0003	0.0007	0.0009	0.0008
0.0002	−0.0068	−0.0075	−0.0072

That mercuric oxide is such a weak base as to have no effect on the alkalinity was demonstrated by measuring the E of the cell.

$$Hg - HgO_{(s)} - KOH\ (0.001\ M) \parallel H_2O - HgO_{(s)} - Hg$$

This cell gave a value of about 0.24 volt, which proves that the mercuric oxide in the right half-cell was not basic enough to interfere with the basic properties of lead oxide. By plotting the measured E of the cell against the logarithm of the molality of potassium hydroxide, a straight line is obtained which cuts the zero line when the activity of OH^- is the same throughout the cell.

In all measurements, a cell will be called positive when there is a tendency for an electron current to flow through the cell from right to left.

The data for this series of cells are given in table 3. By interpolation E is zero when log of molality of potassium hydroxide is -3.735. This gives the molality of potassium hydroxide as 1.84×10^{-4} and therefore the activity of the hydroxide ion in the lead oxide is 1.84×10^{-4}.

A similar series of measurements, table 4, was made with the hydrated oxide, $(PbO)_3H_2O$.

By interpolation the activity of the hydroxide ion in the hydrated lead oxide solution is 2.82×10^{-4}. If this comes from the primary basic ionization of the oxide, it is possible to combine this data with the solubility data in table 1 and calculate the primary basic ionization constant of lead oxide. The activity of the lead ion in such a solution can be estimated from the value -0.122 volt for the Pb—Pb^{++} ($\alpha = 1$) electrode as given in Gerke's (8) compilation of electrode potentials, and the value -0.508 volt for the Pb—$PbO_{(s)} - OH^-$ ($\alpha = 1$) electrode as measured by Smith and Woods (3). By substituting these values in the equation

$$E = E_0 + \frac{0.0592}{2} \log \frac{\alpha Pb^{++}}{1}$$

we get

$$\log \alpha Pb^{++} = \frac{-2}{0.0592} (0.580 - 0.122)$$

$$\alpha Pb^{++} = 3.2 \times 10^{-16}$$

when αOH^- is unity, and the solution is saturated with lead monoxide (red). The solubility of the hydrated oxide is of the same order as the solubility of the red oxide, and we can assume that the product $\alpha Pb^{++} \times \alpha OH^-$ in a $(PbO)_3H_2O$ solution is a number of the order of 3.2×10^{-16}. When αOH^- is 2.82×10^{-4} as given above, αPb^{++} must be about 10^{-8}, which is so small that the secondary ionization of the oxide need not be considered. The ionization constant for the primary ionization $PbO \cdot x\, H_2O \rightleftarrows PbOH^+ + OH^-$ is

$$K = \frac{\alpha PbOH^+ \times \alpha OH^-}{\alpha PbO \cdot x\, H_2O}$$

$$\alpha PbOH^+ = \alpha OH^- = 2.82 \times 10^{-4}$$

$$\alpha PbO \cdot x\, H_2O = 5.75 \times 10^{-4} - 2.82 \times 10^{-4} = 2.93 \times 10^{-4}$$

$$K = \frac{2.82 \times 10^{-4} \cdot 2.82 \times 10^{-4}}{2.93 \times 10^{-4}} = 2.7 \times 10^{-4}$$

The above measurements and calculations indicate that a solution of lead oxide is a true solution, having an ionization constant characteristic of a moderately weak base.

In order to investigate the amphoteric properties of lead oxide and to determine its effect upon the reference electrode, a number of cells of the type

$$Hg - HgO_{(s)} - KOH \parallel KOH - PbO_{(s)} - HgO_{(s)} - Hg$$

were measured. The molality of the potassium hydroxide was the same in each half-cell. These are concentration cells similar to the cells in the previous series and the *E* of the cells will be zero whenever the lead oxide acts equally as an acidic and basic oxide. The data are given in table 5 and the graph in figure 2.

TABLE 5

E M F. of cells $Hg - HgO_{(s)} - KOH \parallel KOH - PbO_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE *E* OF CELL
0 0200	0 0035	0 0036	0 0036
0 0100	0 0017	0 0018	0 0018
0 0075	0 0016	0 0016	0 0016
0 0060	0 0014	0 0015	0 0015
0 0055	−0 0006	−0 0005	−0 0006
0 0050	−0 0027	−0 0021	−0 0024
0 0010	−0 0070	−0 0065	−0 0068

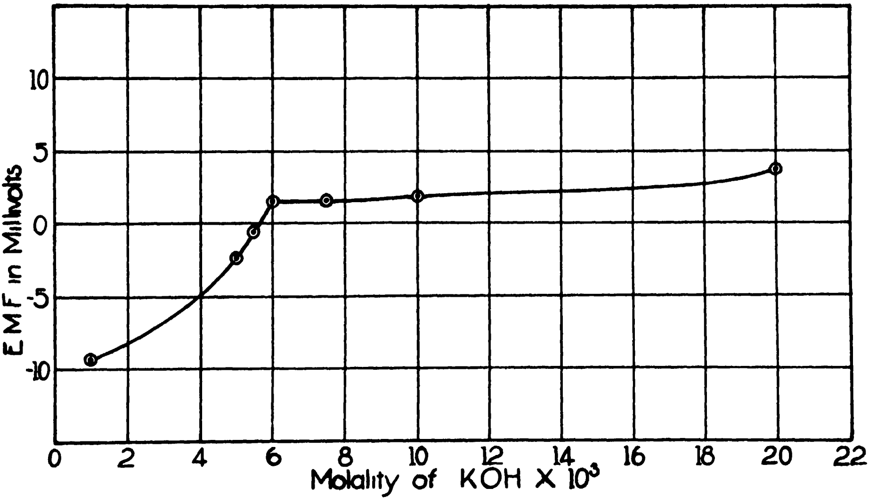

FIG. 2

The data in table 5 prove that in this range of alkalinity, the addition of red lead oxide does not destroy the reproducibility of the electrode. At concentrations of potassium hydroxide greater than 0.02 molal, the potentials showed a greater variation. The molality of potassium hydroxide at which the E curve cuts the zero line, read from figure 2 as 5.6×10^{-3} is called the isoelectric point of the oxide.

SUMMARY

The rate of solubility and the amphoteric properties of lead oxide have been studied, and a general method for measuring the isoelectric point of an amphoteric oxide has been suggested.

REFERENCES

(1) Kuhn: Z. physik. Chem. **114**, 44 (1924).
(2) Simms: J. Am. Chem. Soc. **48**, 1239 (1926).
(3) Smith and Woods: J. Am. Chem. Soc. **45**, 2632 (1923).
(4) Brown, Moss, and Williams: Ind. Eng. Chem., Anal. Ed., **3**, 134 (1931).
(5) Mueller: Z. physik. Chem. **114**, 129 (1928).
(6) Ming Chow: J. Am. Chem. Soc. **42**, 488 (1920).
(7) Randall and Spencer: J. Am. Chem. Soc. **50**, 1572 (1928).
(8) Gerke: Chem. Rev. **1**, 377 (1925).

CERTAIN PHYSICAL PROPERTIES OF DIVINYL ETHER

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Divinyl ether has recently (1) been proposed as an anesthetic. A knowledge of some of its physical properties, and especially of its vapor pressures, was obviously desirable, and a study of certain of these properties is here recorded.

THE MATERIAL USED

A method of preparation of this substance has recently been worked out by Ruigh and Major (2) in the Laboratory for Pure Research of Merck and Company, Inc. They suggested the present work, and we are indebted to them for a sample of their purest product, it being the middle fraction, boiling over a range of 0.02°C., of a freshly prepared and purified batch of over a liter. These investigators show (2) that the product obtained by earlier workers has been of lower purity.

VAPOR PRESSURE MEASUREMENT

This was carried out by the static isoteniscope (3) method of Smith and Menzies. The pressure gauge consisted of a U-form Pyrex glass tube of 13-mm. bore, containing triple-distilled mercury, one limb of which was evacuated to a pressure of less than 0.01 mm. of mercury as measured by a McLeod gauge. The mercury levels were read off against a vertical mirror by means of a truly horizontal hair line ruled on a glass microscope slide fixed in a carrier which could slide the whole length of a graduated vertical steel bar 2½ meters long. The graduation of this bar is nowhere in error by over 0.01 mm. The reduction of the pressure readings to millimeters of mercury at 0°C. and $g = 980.66$ was carried out as described elsewhere (3). At Princeton, $g = 980.18$.

Temperature measurement above 0°C. was made by a mercurial thermometer graduated in tenths of a degree and certificated at the Reichsanstalt to the nearest ±0.02°C. at each 10°C. interval. The ice-point of this thermometer was of course redetermined. Below 0°C. another thermometer graduated to tenths was used, and its readings were corrected, through the courtesy of a colleague, by comparison with a platinum resistance thermometer whose readings are believed good to hundredths of a degree.

The temperature bath was a 4-liter beaker, containing either water or else carbon tetrachloride, adequately stirred by a rotating vertical shaft carrying three propellor-like agitators. By adding solid carbon dioxide the temperature could readily be lowered to −20°C.

In preparing the isoteniscope, we took due precaution to remove, by heating and exhausting, the moisture film from the surface of the glass.

TABLE 1

Vapor pressures of divinyl ether determined experimentally

OBSERVATION NUMBER	T (observed)	PRESSURE (observed)	T (calculated)	$T_{obs} - T_{calc}$
	degrees C	*mm*		
1	−19.70	85.7	−19.673	−.027
2	−19.69	86.0	−19.610	−.080
3	−16.55	101.5	−16.595	.045
4	−16.19	103.5	−16.235	.045
5	−10.02	143.7	−9.986	−.034
6	−9.18	150.0	−9.142	−.038
7	−0.39	230.0	−0.373	−.017
8	−0.04	233.4	−0.060	.020
9	4.06	282.4	4.089	−.029
10	13.58	426.6	13.608	−.028
11	14.01	433.9	14.017	−.007
12	14.39	440.5	14.382	.008
13	20.22	557.2	20.205	.015
14	20.22	557.5	20.218	.002
15	20.56	564.0	20.513	.047
16	20.65	566.7	20.635	.015
17	21.45	584.7	21.434	.016
18	21.79	592.8	21.787	.003
19	21.88	595.8	21.917	−.037
20	22.25	602.9	22.223	.027
21	23.66	636.5	23.636	.024
22	28.35	759.2	28.322	.028
23	28.64	767.0	28.600	.040
24	35.31	971.1	35.183	.127
25	35.64	985.2	35.597	.043
26	43.74	1294.2	43.693	.047
27	43.77	1296.2	43.741	.029
28	43.91	1311.5	44.101	−.191
29	49.33	1551.0	49.361	−.031
30	49.56	1565.7	49.664	−.104

EXPERIMENTAL RESULTS OF VAPOR PRESSURE MEASUREMENT

These are tabulated in table 1, in which the first three columns are self-explanatory.

In order to obtain a smooth curve through our experimental points, we chose a three-constant equation of the Rankine-Kirchoff-Dupré-Hertz type, and evaluated the constants as follows:

$$\log_{10}p_{\mathrm{mm}} = 21\,73592 - \frac{2085\,11}{T_{\mathrm{abs}}} - 4.81530\log_{10}T_{\mathrm{abs}} \qquad \text{(M)}$$

The fourth column in table 1 shows the temperatures calculated for the observed pressures by means of this equation. The fifth column serves to show (1) the closeness of fit, since the algebraic sum of the differences between calculated and observed temperatures is 0.042°C., and (2) the degree of consistence of the observations, for the sum of all the differences, each taken as positive, divided by the number of observations is 0.040°C., which may be considered as the average error of a single observation.

TABLE 2

Vapor pressure of divinyl ether calculated from equation M

	0	2	4	6	8
−30	*46 8*^{3}				
−20	*84 1*^{5}	*75 1*^{7}	*67 0*^{0}	*59 5*^{4}	*52 8*^{9}
−10	143 6	129 5	116 6	104 8	94 0^{1}
−0	234 1	213 0	193 5	177 5	158 9
0	234 1	256 8	281 3	307 6	335 9
10	366 3	398 8	433 6	470 8	511 5
20	552 7	597 7	645 4	696 4	750 2
30	807 3	867 8	931 6	999 1	1070
40	1145	1224	1307	1395	1486
50	*1582*	*1683*	*1788*	*1898*	*2014*
60	*2134*				

Extrapolated values are in italics.

Table 2 shows the vapor pressures of divinyl ether as calculated by equation M for each 2°C. interval from −30°C. to +60°C. We have extrapolated values for 10°C. beyond each end of our experimental range, and show these extrapolated values in italics. We publish these pressure values for such small steps of temperature so that interpolation, using p and t as variables, can be made directly without exceeding the experimental error of the observations.

The normal boiling point of divinyl ether, according to equation M, is 28.35°C. ±0.04°. This is in concordance with the normal boiling point, 28.3°C. ±0.2°, reported by Ruigh and Major.

DÜHRING'S, AND RAMSAY AND YOUNG'S RULE WITH ETHYL ETHER AS COMPARISON SUBSTANCE

Before the present measurements were made, Ruigh had obtained approximate values for the vapor pressures of divinyl ether by comparison with diethyl ether. For very closely analogous substances, the ratio T_V/T_E of the absolute temperatures at which two substances, V and E, have the same vapor pressure should remain approximately constant. At the normal boiling point, this ratio for vinyl and ethyl ethers is 301.45/307.54 or 0.9802. If this ratio is used, employing the values for ethyl ether found in International Critical Tables, the temperature discrepancy from our values for divinyl ether for the pressure 112.3 mm. is −0.50°C. and for the pressure 1277 mm. is +0.12°C. Therefore, not the Dühring but rather the Ramsay and Young equation

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c\,(T'_B - T_B)$$

is to be preferred, where $c = 0.00003$.

DENSITY AND SPECIFIC VOLUME

It is well-known that for ranges of temperature sufficiently removed from the critical temperature, the change of specific volume of a liquid with temperature may be represented satisfactorily by a quadratic equation in t, measured from a convenient point. For ethyl ether, such an equation is said in I. C. T. to represent the facts in the range 0°C. to 70°C. to one part in ten thousand. For our purposes, therefore, it was sufficient to measure the density of divinyl ether at three known temperatures near 0°, +13°, and +25°C. This we did by means of a dilatometer. From the values so obtained, we determined the three constants in the following equation:

$$d_t = [d_s + 10^{-3}\alpha\cdot(t - t_s) + 10^{-6}\cdot\beta\cdot(t - t_s)^2] \pm 10^{-4}\cdot\Delta \qquad \text{(D)}$$

in which $t_s = 0°\text{C.}$
$d_s = 0.79601$
$\alpha = -1.14582$
$\beta = -2.5706$
$\Delta = 2.$

LATENT HEAT OF VAPORIZATION

True values for this can be obtained from the Clapeyron equation, provided dp/dt and the specific volumes of both vapor and liquid are known. Although equation M above is an empirical equation, it nevertheless represents accurately the experimental facts, and we can, therefore, obtain true values of dp/dt by its use. We had already measured the densities of the liquid. It was, therefore, necessary to measure experimentally only the specific volume of the vapor. It is frequently forgotten that values obtained upon the assumption that a saturated vapor follows the simple gas laws may be in error by several per cent. Because the instability of divinyl ether makes it a difficult subject for precise vapor density work, we have contented ourselves with reporting its orthobaric density only at one temperature, the normal boiling point. The measurements were made in a 100-cc. bulb sealed to a graduated capillary in which the condensed liquid portion could be measured with an accuracy of ±0.03 per cent. The total content of divinyl ether in the apparatus was obtained by direct weighing. The orthobaric density of the vapor thus found was 0.00299_4 ±0.5 per cent, a mean of two observations. This value is $5._7$ per cent higher than the value computed by the simple gas laws.

Substituting in the rigid Clapeyron equation the experimental values thus found, we obtain 6260 and 89.4 calories as the latent heat of vaporization of divinyl ether at 28.35°C., per mole and per gram respectively, with an accuracy of ±0.5 per cent.

TROUTON'S CONSTANT

The value just reported yields 20.8 for this constant, as compared with 20.8 for diethyl ether using Mathews' (4) value for the latent heat of vaporization.

HILDEBRAND'S CONSTANT

It will be recalled that Hildebrand (5) found steadier constants than those given by Trouton's rule when he considered entropies of vaporization for series of liquids at temperatures chosen to yield vapors of the same concentration rather than the same vapor pressure. Using the concentration where $\log T - \log p = 0.5$, as in an example studied by Hildebrand, we find that, for divinyl ether, the appropriate temperature is near −21°C. and the constant is 14.2 instead of Hildebrand's standard or average value 13.7. Using Taylor and Smith's (6) values for the vapor pressure of diethyl ether, we find a value of 14.0 for Hildebrand's constant, calculated likewise for the above concentration, which is reached near −17°C.

SUMMARY

The vapor pressures of divinyl ether are reported in the range −30°C. to 60°C.

An equation is given relating experimental values of the density of the liquid to temperature.

The latent heat of vaporization at the normal boiling point is evaluated from the vapor pressure curve with the help of an experimental determination of the orthobaric volume of the vapor.

The constants of Trouton and Hildebrand are evaluated under standard conditions.

REFERENCES

(1) Leake and Chen: Proc. Soc. Exptl. Biol. Med. **28**, 151 (1930).
(2) Ruigh and Major: J. Am. Chem. Soc. **53**, 3663 (1931).
(3) Smith and Menzies: J. Am. Chem. Soc. **32**, 1419 (1910).
(4) Mathews: J. Am. Chem. Soc. **48**, 562 (1926).
(5) Hildebrand: J. Am. Chem. Soc. **37**, 970 (1915).
(6) Taylor and Smith: J. Am. Chem. Soc. **44**, 3450 (1922).

ARE LIQUID SODIUM AMALGAMS COLLOIDAL?

A DISCUSSION OF THE PAPER OF PARANYPE AND JOSHI

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A recent issue of This Journal (1) contains an article by Paranype and Joshi which presents arguments purporting to show that sodium amalgams are colloidal in nature and that as such their properties depend on the method of preparation and treatment as well as on the concentration. If the conclusions of these authors are correct, most of the experimental data on sodium amalgams, and by implication the data on all of the alkali metal amalgams, become of doubtful value since in most cases the physical method of handling the amalgams has not been considered a significant factor. It would seem, therefore, worth while to analyze carefully the arguments of Paranype and Joshi and to present further evidence as to the nature of these solutions.

Two questions have been raised by Paranype and Joshi. First, does the method of preparing an amalgam affect the physical properties or is it sufficient to know the concentration, temperature, and pressure? Second, are sodium amalgams colloidal solutions? The answer to the first question does not necessarily answer the second, since it is possible that a reversible colloid might exist. The data and arguments presented by Paranype and Joshi will first be discussed and finally additional data which permit rather definite conclusions will be presented.

THE REPRODUCIBILITY OF AMALGAMS

Paranype and Joshi enumerate five different types of experimental data in which the results do not seem to be reproducible. They conclude that the different methods used in preparing the amalgams resulted in different colloidal solutions and account in this way for the experimental data. Let us consider these cases in detail. The data on the conductivity of amalgams obtained by Hine (2), Vanstone (3), Bohariwalla (4), and Davies and Evans (5) are described as follows: "Hine finds that the conductance of sodium amalgam passes through a minimum; Vanstone states that the conductivity concentration curve exhibits a maximum corresponding with $NaHg_2$; Bohariwalla and others obtain two discontinuities, one at 0.079

per cent Na and one at 0.272 per cent Na; while Davies and Evans report only one at 0.272 per cent Na." This treatment does not seem to give a correct picture of the facts. As a matter of fact the first, third, and fourth of these papers agree within the limits of experimental error. The agreement is far from perfect, but seemed to the original investigators satisfactory. Thus, to quote Davies and Evans, "It is difficult to decide with certainty whether these discontinuities in the curves are real, owing to the experimental difficulties;" and again, referring to their work and that of Hine, "It is seen that on the whole the results are in fairly good agreement." Bohariwalla states, "These breaks in the conductivity concentration curves in the case of sodium and potassium amalgams occur at the same composition as have been found by Hine." These data refer to amalgams of from 0 to 5 atom per cent sodium. Vanstone, on the other hand, was working with amalgams containing from 50–100 atom per cent sodium, and therefore his paper is quite irrelevant to the point in question.

The second instance of marked variation in properties has to do with the reactivity of amalgams prepared by Willstätter, Seitz, and Bumm (6) in iron, porcelain, or hessian crucibles. Since Willstätter considered the impurities present sufficient to account for the difference in the behavior of these amalgams, this does not seem to be evidence that pure amalgams have properties which depend on the method of preparation.

The next data to be discussed are those obtained by Vanstone for the phase diagram of sodium amalgams. Paranype and Joshi state, "At all concentrations he observed persistent superfusion and supercooling, which indicates that the freezing point of an amalgam is not definite but extends over a small range of temperature." This conclusion seems to be based on the rather unusual use of the word, "superfusion." The following quotation from Vanstone indicates that the phenomenon observed is nothing more than ordinary supercooling. To quote Vanstone, "The alloy was heated until entirely liquid, then allowed to cool slowly, meanwhile being vigorously stirred. The temperature was read every minute or half minute. In nearly all cases superfusion was observed and the points determined are the maximum temperature reached after overcooling." Nothing is said by Vanstone about heating curves, and we must therefore conclude that he is using the term "superfusion" as synonymous with supercooling. Supercooling is so commonly found for true solutions and pure compounds that it can not be taken to mean that there is any uncertainty regarding the melting point or transition temperature.

The fourth argument has to do with the uncertainty in the composition of the solid phase deduced from the phase diagram. This uncertainty arises chiefly from the fact that the curve is very steep in certain parts and there are many breaks in the curve. For example, in dilute solution Kurnakow states that it is uncertain whether the compound is $NaHg_6$ or

$NaHg_6$, while Schüller and Vanstone state that the compound is probably $NaHg_4$. It must be emphasized, however, that the disagreement is in the interpretation of the data and not in the data itself. These authors found the break in the temperature concentration curve at 17.95, 18.1, and 17.9 per cent sodium which is quite good agreement. The fact that the experimental data is of such a nature as to make the *authors* of these papers uncertain as to the composition of the solid phase does not indicate that the *solid phase* is of uncertain composition.

The last argument has to do with the change of viscosity of sodium amalgams with the time. The experimental work was carried out in the laboratory of Paranype and Joshi in 1928 but has never been published. In the absence of information regarding the methods of obtaining the data it is difficult to draw conclusions as to its significance. A possible explanation would be that the concentration of the amalgam was changing, owing either to surface oxidation or perhaps to incomplete solution of the solid amalgam, which melts at nearly 360°C. Since Paranype and Joshi state in another connection that their amalgams exhibit a scum on the surface when left in contact with their purest nitrogen perhaps the first of these explanations is the more probable. At any rate Paranype and Joshi come to the conclusion, in discussing other properties of amalgams, that they are lyophilic colloids. That the viscosity should increase with shaking is certainly not characteristic of lyophilic colloids and would indicate again that some other explanation must be sought for the viscosity data.

The above discussion leads to the conclusion that experiments cited by Paranype and Joshi do not indicate that the method of preparing pure sodium amalgams is of significance.

COLLOIDAL SOLUTION

The second proposition to be discussed is the question whether amalgams are colloidal or true solutions. Even though the method of preparing amalgams is of no significance, these solutions might be colloidal or partly colloidal. If such a solution were in mobile equilibrium it might be colloidal and still give properties determined by only the concentration temperature and pressure. This question cannot be answered with certainty, but one can scrutinize the arguments for and against the colloidal nature of the solution.

The argument of Paranype and Joshi in so far as it is based on the irreproducibility of the properties of amalgams has been discussed in the first part of this paper. They also give as evidence the fact that the transfer of sodium with the electric current is toward the cathode in concentrated amalgams and toward the anode in dilute solutions, thus resembling the behavior of certain colloidal solutions. If the colloid explanation were the only one possible this would have to be considered an argument. As stated by Paranype and Joshi, however, there are several other possible explanations, so that one cannot consider this by itself as proof.

Several experimental facts are cited (the effect of ultra-violet light on amalgams, the viscosity and surface tension) to prove that the solution cannot be a lyophobic colloid. These are of course of interest after one has concluded that the solutions are colloidal, but do not either prove or disprove this point.

Paranype and Joshi also say that they would expect the solid phase to be crystalline, the heat of solution to be very large, and the vapor pressure of mercury to be less than would be calculated for true solution. These are certainly not attributes of ordinary lyophilic colloids and to say the least do not suggest the colloidal state.

The fact that direct and alternating current measurements give the same value for the conductivity seems to be of no significance, inasmuch as practically all of the conductivity is electronic. Thus it has been shown (7) that the transference number of sodium in these amalgams is less than 10^{-5}. Conductance data would have to be precise to one part in one hundred thousand in order to give much information regarding the behavior of sodium. The data at hand do not begin to approach this degree of precision. If for no other reason than this, the conductance data are not significant in this connection.

In commenting on the work of Richards and Conant (8), Paranype and Joshi state that the deviations from the laws of ideal solution are to be attributed to either colloidal solution or experimental error. Were this true, practically all solutions would have to be considered colloidal, particularly aqueous solutions of strong electrolytes. The object of the experiments of Richards and Conant was to study a solution which gave large deviations from the laws of ideal solution, but they certainly had not the slightest thought that these deviations were due to "experimental error," or that they were due to the colloidal nature of the amalgams.

Finally the suggestion that the formation of scum on the surface of an amalgam is not always due to the formation of oxide but may be due to the disperse phase separating out on the surface, seems to be an argument based on faulty experimental data. Amalgams have frequently been kept for years by the writer in flasks which have been highly evacuated and baked to remove adsorbed water and during such intervals of time showed not the slightest tract of scum.

We may conclude, therefore, that no evidence has been presented which would justify one in concluding that these amalgams are colloidal. This, however, does not prove that amalgams are true solutions. There is some evidence, however, pointing toward true solutions. Perhaps the most convincing is to be found in vapor pressure data. It has been shown (9) that the vapor pressure curve in dilute solutions is that calculated from Raoult's law, thus indicating that we are dealing with single atoms of sodium as the solute. These atoms of course may be solvated, but this would not constitute a colloidal solution as suggested by Paranype and Joshi. To quote them, ". . . . Lewis, Adams, and Lanman formulated a theory and explained the initial decrease in conductivity . . . . as due to large aggregates of mercury atoms gathering around a sodium atom . . . . This conception of Lewis and coworkers appears to be very similar to the formation of a solutoidal colloid." One might infer from this statement that the hydration of ions in water solution is proof that aqueous solutions of strong electrolytes are colloidal.

The freezing point lowering in dilute amalgams is that calculated from Raoult's law. The calculated value is 1.9°C. per atom per cent and the experimental value is 1.9 (3), increasing in more concentrated solutions. A colloidal solution would give a smaller depression of the freezing point.

The excellent microphotographs of Vanstone, which show several types of crystals corresponding to the compounds indicated by the phase diagram, indicate that the solid phase is not colloidal.

The large heat of solution indicates that we cannot be dealing with a lyophobic colloid in which the disperse phase is sodium. Such a colloid would have a greater amount of energy in the form of surface energy instead of much less energy than the original components.

This leaves the possibility of a lyophilic reversible colloid in rather concentrated liquid amalgams. This is only a possibility, however, and until there is positive evidence one is bound to consider it as only a possibility.

SUMMARY

1. Contrary to the conclusion of Paranype and Joshi, there is no proof that the properties of pure sodium amalgams are determined by the method of preparation.

2. The hypothesis that sodium amalgams are colloidal rests upon certain properties which are common to the amalgams and to certain colloidal solutions. Since these properties can be accounted for in other ways, there is no proof at present that sodium amalgams are colloidal.

3. The following facts either prove or constitute strong evidence that sodium amalgams are true solutions.

(a) The freezing point depression of mercury in dilute amalgams is that calculated for an ideal solution.

(b) The vapor pressure lowering is that calculated for an ideal solution. In more concentrated amalgams the lowering is greater than is calculated for an ideal solution. A colloidal solution should show a smaller lowering of the vapor pressure.

(c) The microphotographs of Vanstone of the solid phases indicated by the phase diagram show definite crystalline structure.

(d) The large amount of heat liberated during the formation of an amalgam proves that it cannot be a lyophobic colloid in which the disperse phase is sodium.

REFERENCES

(1) Paranype and Joshi: J. Phys. Chem. **36**, 2474 (1932).
(2) Hine: J. Am. Chem. Soc. **39**, 882 (1917).
(3) Vanstone: Trans. Faraday Soc. **9**, 291 (1914).
(4) Bohariwalla: Indian J. Physics **4**, 147 (1929).
(5) Davies and Evans: Phil. Mag. [7] **10**, 569 (1930).
(6) Willstätter, Seitz, and Bumm: Ber. **61B**, 871 (1928).
(7) Lewis, Adams, and Lanman: J. Am. Chem. Soc. **37**, 2656 (1915).
(8) Richards and Conant: J. Am. Chem. Soc. **44**, 601 (1922).
(9) Bent and Hildebrand: J. Am. Chem. Soc. **49**, 3011 (1927).

PRIMARY SALT EFFECTS IN REACTIONS IN WHICH THE SUBSTRATE IS NEUTRAL

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It has been suggested by some authors (1) that the primary salt effects in reactions between an ion and an uncharged molecule are governed solely by the changes in the activity coefficient of the catalyzed molecule produced by salt addition. However, as already pointed out by Harned and Åkerlöf (2), experimentally determined values of f_B, the activity coefficient of the neutral substrate, account for neither the order nor the magnitude of the velocity constant variations in salt solutions. In this brief communication a new method of approach will be discussed.

Harned (3), in calculating the activity coefficients of hydrochloric acid in HCl–MCl solutions, has employed the equation

$$\log f = \frac{-.354\sqrt{2C_T}}{1 + A\sqrt{2C_T}} + 2B_a \cdot c_a + 2B' \cdot c_s \tag{1}$$

B′ is an empirical constant characteristic of the salt. Butler (4), by considering the mutual salting-out of ions obtained an expression which may be used in the interpretation of the B constants. Carrying this idea further we may look upon the B' constant as determining the displacement, or salting-out, of the acid by the salt—inasmuch as in an HCl–MCl solution we have the displacement of hydrochloric acid not only by its own ions but also by the ions of the added salt—and use the Debye and MacAulay (5) expression to represent this part of the activity coefficient. A comparison of the proposed expressions for B and B' leads immediately to the relation

$$B' = B_a \frac{a_{\text{acid}}}{a_{\text{salt}}} \tag{2}$$

a, the mean ionic radius, is defined by

$$\frac{1}{a} = \frac{1}{\Sigma \nu_i z_i^2}\left[\frac{\nu_+ z_+^2}{a_+} + \frac{\nu_- z_-^2}{a_-}\right] \tag{3}$$

As the values of B' have been computed by Harned from thermodynamic measurements by means of equation 1, it is possible to test equation 2;

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the agreement is quite satisfactory. Although it is doubtful whether B and B' as determined empirically from equation 1, are independently correct, and whether the Butler, and the Debye and MacAulay equations separately express completely these constants, equation 2 may be taken to be valid, as any other factors that may enter will be common to both B and B'; the recently published thermodynamic data of Hawkins (6) also support this equation, in spite of the fact that the B and B' values given differ somewhat from those of Harned. It is also interesting to note that B', being a partial, must be related to the B constants of both the salt and the acid; this relation for HCl–MCl solutions, using the data of Harned (7), is found empirically to be a very simple one.

$$B' = \frac{B_a + B_s}{2}$$

The introduction of the B' constants, as calculated from equations 2 and 3—the ionic radii values are those calculated from crystallographic data (8)—in the interpretation of primary salt effects, for the type of reaction considered, has led to interesting results, it being possible to account for the salt effects in all but one of the reactions examined. Because of the complexity of the problem, no strict theoretical justification can be given for this linking. We may, perhaps, regard the salting-out of a strong, highly soluble electrolyte as its displacement from the neighborhood of the ions of the added salt and therefore as its increased ability to collide with the substrate molecules to form the complex capable of decomposition. Further, it can be shown, from the empirical relation for a uni-univalent electrolyte

$$B' = \frac{B_a + B_s}{2}$$

together with the expressions for B and B', that the displacement coefficient may be also regarded as the change in the dielectric constant, provided that the mean of the δ's (δ is the molal lowering in the dielectric constant) as well as of the a's (defined by equation 3) for the catalyst and the salt is employed; this explanation would be in accord with the suggestion of Harned and Samaras (9).

It is known from experimental data that for reactions between an ion and an uncharged molecule the interionic-force term of the Debye and Hückel expression does not appear, the logarithm of the rate constant varying linearly with the salt concentration (the concentration of the catalyst being fixed) up to very high concentrations (6 or $7N$); if, of course, both the ions of the catalyst exert a catalytic effect, this term does enter. The results of the present investigation are summarized in table 1.

That the characteristic factors by which the displacement coefficients

TABLE 1

Expressions for the primary salt effects

REACTION	CATALYST	SALT EFFECT
Cane sugar hydrolysis (i)	H^+	$\log k = 3B'\cdot n_s + R$
Acetylchloroaminobenzene transformation (ii)	H^+ and Cl^-	$\log k =$ (interionic-force effect) $+ 3B'\cdot n_s + R^{I}$
Cyanamide hydrolysis (iii)	H^+	$\log k = 2B'\cdot n_s + R^{II}$
Hydrogen peroxide decomposition (iv)	I^-	$\log k = 2B_s\cdot n_s + R^{III} \approx 4B'\cdot n_s + R^{III}$
Diacetone alcohol decomposition (v)	OH^-; cation also?	$\log k =$ (interionic-force effect) $- 2B'\cdot n_s + R^{IV}$
Ethyl acetate hydrolysis (vi)	H^+	$\log k = \frac{1}{2} \log f_s + R^{V}$

R is a constant independent of the salt but characteristic of the reaction. The term involving B' is in each case the displacement coefficient of the catalyst. The salt concentrations are from about 0.4*N* to the highest concentration for which data are available. The salt effects are represented very satisfactorily by the expressions given.

(i) The salt data for this reaction are those of Kautz and Robinson (10), and for the medium effect in pure hydrochloric acid (i.e., for the slope of the log $\frac{k}{n_{HCl}}$ vs. n_{HCl} line) those of Worley (11).

(ii) The empirical equation used by Åkerlöf (12) has been simply rewritten.

(iii) The values of the slopes of the log $\frac{k}{k_0}$ vs. n_{salt} lines as given by Grube and Schmid (13) have been used. As neither the *B* constant for nitric acid nor the ionic radius of the nitrate ion is known, equation 2 cannot be employed, and the assumption has been made that the displacement coefficients of nitric acid in HNO_3–MNO_3 solutions are the same as those for hydrochloric acid in HCl–MCl solutions, which is perhaps justifiable as in the hydrolysis of sucrose it is found from the data of Worley that the medium effect for nitric acid is exactly the same as that for hydrochloric acid.

(iv) Harned and Samaras (9) have shown that for the hydrogen peroxide decomposition the salt effects can be interpreted by the *B* constants of the added salts; although B_{KI} is not known, by using the empirical relation $B' = \frac{B_{catal.} + B_{salt}}{2}$ together with equation 2, its value may be calculated to be nearly zero (which seems to be borne out also by activity coefficient curves), so that the partial B', which includes both the *B* for the catalyzing electrolyte and the *B* for the salt, will in this case involve B_s alone.

(v) The B''s employed are those of Harned and Åkerlöf (7a), as the calculation from equation 2 cannot be carried out, since the radii of the hydroxides are not known. The catalytic data are those of Åkerlöf (14) and the agreement obtained by using the equation given in the above table is remarkably good up to 6*N* salt concentrations.

(vi) Robinson (15) showed that the *square root* of the activity coefficient of the ethyl acetate accounted for the salt effects; it is possible, although highly doubtful as the order for the various salts is different, that $\log f_s$ is related to the B' constant. As this is the only one of the reactions examined for which the salt effects are given by $f_s^{\frac{1}{2}}$, we must regard it for the present as complicated by an unknown factor or factors.

are multiplied appear to be whole integers, as seen from table 1, must not be regarded as significant, in view of the uncertainty of the values of many of the fundamental quantities involved; all that may be claimed is that the B' constants account quite well for the greatest part of the salt effect. If we agree with Brönsted (16) and Bjerrum (17) that some kind of a complex is formed, we should expect to deal with a ratio of two displacement coefficients, so that for a reaction between an ion and an uncharged molecule and for uni-univalent salts we shall have,

$$\log \frac{k}{k_0} = 2[B_i' - B_x']\cdot n_s \tag{4}$$

It may be shown that if the susceptibility, α, of the complex is greater than that of water, then the slope of equation 4 is positive and greater than $2B_i'$; similarly, the negative sign in the diacetone alcohol reaction may be accounted for on the assumption that $\alpha_x < \alpha_{OH} < \alpha_{H_2O}$. This scheme is by no means new, as the Brönsted (16) expression, assuming that A in equation 1, which involves the so-called mean distance of approach of the ions, is the same for the catalyst as for the complex, would lead to

$$\log \frac{k}{k_0} = [\beta_i - \beta_x + \beta_B]\cdot n_s \tag{5}$$

Equation 5 differs from equation 4 in that it involves the activity coefficient of the uncharged molecule; it should be pointed out, however, that the values of β_B, as determined from solubility measurements, are not of the same order as the B' constants, and it consequently appears that the kinetic factor F, given by the well-known expression,

$$v = k\cdot c_i c_B \cdot F$$

does not involve the activity coefficient of the neutral substrate.

A comprehensive and detailed examination of this field leads one to the realization that an exact theoretical treatment is impossible at present, not only because of the inherent complexity and obscurity of the problems of chemical reactivity and highly concentrated solutions, but also owing to the paucity, if not complete absence, of reliable data on such fundamental quantities as the dielectric constants of salt solutions. Nevertheless, it is hoped that the viewpoint presented here, supported as it is by experimental data, may be of some value in the final analysis of the problem.

The writer is indebted to Professor H. S. Harned for valuable assistance and information.

REFERENCES

(1) SCATCHARD: Chem. Rev. **10**, 237 (1932).
GROSS: Monatsh. **53–54**, 445 (1929).
(2) HARNED AND ÅKERLÖF: Trans. Faraday Soc. **24**, 666 (1928).
(3) HARNED: J. Am. Chem. Soc. **48**, 325 (1926).
(4) BUTLER: J. Phys. Chem. **33**, 1015 (1929).
(5) DEBYE AND MACAULAY: Physik. Z. **26**, 22 (1925).
(6) HAWKINS: J. Am. Chem. Soc. **54**, 4480 (1932).
(7) HARNED AND ÅKERLÖF: Physik. Z. **27**, 411 (1926).
HARNED: J. Am. Chem. Soc. **51**, 416 (1929).
(8) PAULING: J. Am. Chem. Soc. **49**, 765 (1927); that for the H^+ is the one given by BRAGG: Phil. Mag. [6] **40**, 169 (1920).
(9) HARNED AND SAMARAS: J. Am. Chem. Soc. **54**, 9 (1932).
(10) KAUTZ AND ROBINSON: J. Am. Chem. Soc. **50**, 1022 (1928).
(11) WORLEY: J. Chem. Soc. **99**, 349 (1911).
(12) ÅKERLÖF: J. Am. Chem. Soc. **49**, 2955 (1927); the equation used by Åkerlöf as given in this paper contains two typographical errors.
(13) GRUBE AND SCHMID: Z. physik. Chem. **119**, 19 (1926).
(14) ÅKERLÖF: J. Am. Chem. Soc. **48**, 3046 (1926).
(15) ROBINSON: Trans. Faraday Soc. **26**, 217 (1930).
(16) BRÖNSTED: Chem. Rev. **5**, 231 (1928).
(17) BJERRUM: Z. physik. Chem. **108**, 82 (1924); **118**, 251 (1925).

STUDIES IN COPRECIPITATION. IV

THE COPRECIPITATION OF ALKALI IONS WITH CALCIUM OXALATE AND THE ADSORBENT PROPERTIES OF THE LATTER[1]

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In a previous general discussion (1) of the phenomena of coprecipitation, the presence of foreign ions in the interior of a precipitate was quite generally ascribed to an adsorption of these ions during the growth of the crystalline precipitate. Therefore it may be expected that the order of the amount of coprecipitation in a series of cations or anions, respectively, will be the same as the order of adsorption at the external surface of the precipitate after it has been formed. In order to prove this conclusion, the adsorption of various electrolytes by aged calcium oxalate crystals has been determined. This study is preliminary in character. Many difficulties, especially of analytical nature, have been encountered, which have not yet been completely overcome; therefore a more extensive investigation of the adsorbent properties of calcium oxalate is reserved for the future. The results obtained in the present study are conclusive insofar as the relation between adsorbability and coprecipitation of ions is concerned.

According to the Paneth-Fajans adsorption rule, the adsorbability of a salt having an ion in common with the crystalline adsorbent should increase with decreasing solubility of the salt. J. S. Beekley and H. S. Taylor (2) in a study of the adsorption of silver salts by silver iodide obtained results in fair harmony with this rule; the agreement would have been still better if they had considered the deformation of the adsorbed anions. It follows from the Paneth-Fajans rule that the adsorbability of any individual ion will be larger the smaller the solubility of the compound that it can form with the ion of opposite charge in the adsorbing lattice. This conclusion, however, is not confirmed by the work of Sven Odén (3) and Mlle. L. de Brouckère (4); a more exhaustive discussion must be postponed until more experimental data are available.

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[1] The material covered in this and following papers has been taken from a thesis submitted by E B Sandell (Du Pont Fellow in Chemistry at the University of Minnesota, 1931–1932) to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ADSORPTION OF ELECTROLYTES BY CALCIUM OXALATE

Preparation of aged calcium oxalate suspensions

Preparation I. 0.515 mole of calcium chloride hexahydrate dissolved in 1 liter of hot water was added slowly over a period of twenty minutes to 0.50 mole of ammonium oxalate dissolved in 3 liters of solution at 90°C. The precipitate was washed by decantation until washings were entirely chloride-free. The precipitate contained traces of chloride that could not be washed out; the amount did not exceed 0.01 per cent. The preparation was allowed to stand under water for a week before use in the adsorption experiments. The average crystal diameter was estimated to be 0.5 micron or less.

Preparation II. Precipitation was made in the same way as described under Preparation I, with the sole difference that at the end of the precipitation ammonium oxalate was a few per cent in excess. The preparation was washed by decantation thirteen times and kept under water for two weeks before being used. The average crystal diameter was estimated to be 0.5 micron or slightly more.

Preparation III. 1.00 mole of calcium chloride in 1 liter of hot water was added in a slow stream to 1.02 moles of ammonium oxalate in 3 liters of boiling water containing 2 cc. of hydrochloric acid. The time of addition was fifteen minutes. The precipitate was washed by decantation twelve times. It was kept under water for two months before using. The crystal size was slightly larger than in the preceding preparations.

Procedure

The carefully washed precipitate was mixed with water to give a suspension containing approximately 3 g. of calcium oxalate in 50 cc. From this suspension, well shaken, 50 cc. were removed with a pipet and transferred to a dry glass-stoppered bottle. Then 50 cc. of the solution containing the substance to be adsorbed were mixed with the suspension, and the whole was agitated in a mechanical shaker. The time of shaking is recorded in table 1. The adsorption took place at room temperature, 25±2°C. Because of the uncertainty involved in determining the small amount of substance adsorbed, the use of a thermostat was considered superfluous. After shaking, the mixture was filtered through paper, and 50 cc. of the filtrate was removed with a pipet and titrated with the suitable standard solution. In the case of the oxalates, 0.02 *N* potassium permanganate was used. The end-point correction was obtained by adding potassium iodide to the cold titrated solution and titrating the liberated iodine with 0.005 *N* sodium thiosulfate in the usual manner. The original solution containing the substance to be adsorbed was standardized in exactly the same way by taking 25 cc. In the case of the adsorption of iodates, 0.02 or 0.002 N sodium thiosulfate served for titrating the iodine liberated by adding iodide to the acidified solution, starch being used as indicator. Bromate was titrated in the same way. For the titration of hydrochloric acid and oxalic acid, dilute carbonate-free sodium hydroxide was used. All salts used in the adsorption determinations were of the highest purity. The oxalate solutions were prepared immediately before use to preclude the formation of carbonate by photochemical decomposition. The results of these experiments will be found in table 1.

TABLE 1

Adsorption by calcium oxalate monohydrate

SOLUTION	TIME OF AGITATION	EQUILIBRIUM CONCENTRATION	MICROMOLES ADSORBED PER GRAM OF CALCIUM OXALATE MONOHYDRATE		
			Preparation I	Preparation II	Preparation III
	hours	*molarity*			
Ammonium oxalate	1	0.0100	5.5	3.7	1.3 (3 hours)
Potassium oxalate	1	0.0100		4.8	2.7 (3 hours)
Sodium oxalate	1	0.0100	9.3	7.5	3.9
Sodium oxalate	3	0.0100	9.8	7.2	3.9
Lithium oxalate	1	0.0100		3.5	
Magnesium oxalate	1	0.0014	6.5		
Oxalic acid	1	0.0100	6.0 (Ox^{-})	7.9 (Ox^{-})	
Oxalic acid	3	0.0100	6.2 (Ox^{-})	8.0 (H^{+})	3.6 (Ox^{-})
Ammonium iodate	1	0.00100		0.73	
Potassium iodate	1	0.00100	0.58	0.95	
Potassium iodate	1	0.0100	5.2	4.3	
Sodium iodate	1	0.00100		0.86	
Lithium iodate	1	0.0100		4.6	
Calcium iodate	1	0.00100	1.7	1.7	
Calcium iodate	3	0.00100	1.7		
Iodic acid	1	0.00100		1.32 (IO_3^-)	
Iodic acid.	2	0.00100		1.57 (IO_3^-)	
Iodic acid.	2	0.00082		18.0 (H^+)	
Potassium bromate	1	0.0100		2.0	
Sodium oxalate + sodium iodate	1	0.00100 0.00100		0.14 (IO_3^-)	

The millimoles of substance adsorbed per gram of calcium oxalate monohydrate equals

$$\frac{NF}{W}\left[V_2 - V\frac{(V + 50.00)}{50.00}\right]$$

where N = the analytical normality of the solution used for titration,
F = conversion factor (NF = molarity of solution of adsorbed ion),
V_2 = cc. of standard solution required to titrate 50.00 cc. of solution containing substance to be adsorbed,

V_1 = cc. of standard solution required to titrate 50.00 cc. of filtrate after equilibrium,

V_s = cc. of water in 50.00 cc. of calcium oxalate suspension (determined by weighing 50.00 cc. of suspension and deducting from this value the weight of calcium oxalate monohydrate obtained by evaporating the suspension to dryness and heating the residue at 105°C.), and

W = grams of calcium oxalate monohydrate in 50.00 cc. of suspension.

DISCUSSION OF RESULTS

The adsorption of alkali oxalates by aged calcium oxalate is very small in amount. Even with the fine precipitates used in these determinations it is not easy to obtain reproducible results. The most strongly adsorbing preparation of calcium oxalate in equilibrium with 0.02 *N* sodium oxalate, the alkali oxalate most strongly adsorbed, contains less than 0.1 per cent of its weight of the foreign oxalate on the surface. It is evident that from the analytical point of view external adsorption cannot play any important rôle in the contamination of calcium oxalate, especially when it is remembered that even this small amount of adsorbed substance is partly removed on washing the precipitate. In analytical precipitations the crystals are much larger than those used in these experiments, so that in considering the causes of contamination, it is possible to leave out of sight entirely that due to external surface adsorption.

The order of adsorption of the oxalates at room temperature at the same equilibrium concentration appears to be as follows: lithium < ammonium < potassium < oxalic acid, sodium < magnesium. Evidently the solubility of the oxalates does not alone determine the adsorbability, for then the order would be: potassium < oxalic acid < lithium < ammonium < sodium < magnesium. (Solubilities of oxalates: potassium 1.65, lithium 0.61, ammonium 0.39, sodium 0.28, magnesium 0.0020, oxalic acid 0.81 moles per thousand grams of water at 25°C.) Ammonium oxalate especially seems to be out of place. In agreement with the order of adsorbability, the amount of coprecipitation increases in the order ammonium < potassium < sodium < magnesium, as will be shown later. The mechanism of the adsorption of oxalic acid probably is somewhat different from that of the salts, since there is a possibility that some of it may be held at the surface in the form of bioxalate ions. In addition, it should be mentioned that the amount of iodic acid adsorbed, as found from the acidimetric determination, is much larger than that found from the iodate analysis. The explanation is that the preparation of calcium oxalate used contained coprecipitated calcium hydroxide, which was neutralized by the hydrogen ions. It was experimentally proved that in the case of hydrochloric acid and of iodic acid, more calcium than oxalate went into solution when calcium oxalate was shaken with the acids, thus indicating that calcium hydroxide existed on the surface of the precipitate and that this reacted with the hydrogen ions. Therefore, the results of acidimetric analysis cannot be used here for obtaining the amount of acid adsorbed. It is possible that the inequality in the adsorption of the two ions is partly to be attributed to an exchange adsorption between hydrogen and calcium ions.

Calcium iodate is more strongly adsorbed than the alkali iodates, as would be expected from the precipitation rule. From 0.001 molar solutions the adsorption of the alkali iodates is of the same order of magnitude; more work should be done over a wider range of concentrations in order to learn whether sodium iodate is more strongly adsorbed than potassium iodate, and the latter more strongly than ammonium iodate. From the figures in table 1, it will be seen that the adsorption of the alkali iodates increases very strongly with the concentration up to an equilibrium concentration of at least 0.01 molar. Since calcium iodate is much less soluble than calcium bromate (0.0078 and 3 moles per thousand grams respectively at 25°C.) a stronger adsorption of the former ion was anticipated. In agreement herewith a much stronger adsorption of potassium iodate than of bromate was found (Preparation II). Again, it was found in the study of the coprecipitation of anions that iodate is carried down to a much greater extent than bromate, if the precipitations are made under identical conditions.

Very interesting is the result of the experiment in which calcium oxalate was shaken with a mixture of sodium oxalate and sodium iodate containing 0.001 moles of each per liter. Although the amount of iodate adsorbed is six times less than in the absence of oxalate, it is evident that the latter is not able to replace all adsorbed iodate at the surface of the calcium oxalate. There is competition between the oxalate and iodate ions and since calcium oxalate is less soluble than calcium iodate, the former ion will be more strongly adsorbed than the latter, although oxalate is not able to prevent entirely the adsorption of the anion which is foreign to the lattice. The adsorbability is not determined by the fact whether the ion is identical with, or of the same size as, that of the same sign in the lattice. The result found explains why a coprecipitation of iodate or some other anion is found if, during the precipitation of calcium oxalate, an excess of oxalate ions is present in the solution, and why cations can be coprecipitated even if there is an excess of calcium present during the precipitation. The presence of the lattice ion does not entirely prevent the adsorption of foreign ions of the same sign.

COPRECIPITATION OF THE ALKALIES WITH CALCIUM OXALATE

The contamination of calcium oxalate by the alkalies was studied under the following heads:

1. Coprecipitation of alkali—sodium, potassium or ammonium—when the corresponding oxalate was used as a precipitant for calcium chloride. The results are given in table 3.
2. Special investigation of sodium coprecipitation. Sodium was present here as the chloride, not the oxalate, and ammonium oxalate was used as the precipitant for calcium. The results are given in table 4.
3. Investigation of alkali coprecipitation under analytical conditions. Ammonium oxalate was used as precipitant; the alkalies were present as chlorides. The results are given in table 5.

Methods of determining the alkalies in the calcium oxalate precipitate

Sodium. This cation was determined by the simple method of Barber and Kolthoff (5). The presence of calcium as chloride does not interfere in the procedure given by these authors, so that their directions have been followed with minor changes to better accommodate the method to the present problem of determining sodium in calcium oxalate. The calcium oxalate precipitate was first dried and then ignited at incipient red heat to convert it to calcium carbonate. The latter was dissolved in dilute acetic acid; the excess acid was removed by heating at 100°C. until solid calcium acetate remained. To the residue was added 10 cc. of zinc uranyl acetate reagent prepared according to the directions of Barber and Kolthoff. The resulting mixture was shaken until all the calcium acetate had been dissolved and was then allowed to stand overnight to insure the complete separation of the small amounts of sodium present. The precipitate was collected in a sintered glass filtering crucible and washed successively with the reagent and a saturated alcoholic solution of sodium zinc uranyl acetate; after washing several times with ether, it was dried by passing a stream of air through the crucible for five minutes and then weighed. Blanks with calcium oxalate to which had been added known small amounts of sodium gave satisfactory results. Only one small source of difficulty was encountered; sometimes after the ignition of the calcium oxalate, the residue contained small amounts of carbon. However, this substance could be removed by repeatedly evaporating the residue with small amounts of concentrated nitric acid.

Potassium. It is not easy to determine the potassium content of contaminated calcium oxalate precipitates. Sodium cobaltinitrite, the most sensitive precipitant for potassium, was chosen as the reagent most likely to give results satisfactory for the present purpose. The method finally adopted consisted in weighing the air-dried precipitate of sodium potassium cobaltinitrite formed in alcoholic solution. The determination was made in the following manner.

The washed and dried calcium oxalate precipitate was ignited at dull redness to convert it entirely to the carbonate. The residue was dissolved in a slight excess of hydrochloric acid and the resulting solution was evaporated to dryness. The calcium chloride residue containing the traces of potassium sought was dissolved in 5 cc. of 95 per cent alcohol at room temperature. When complete solution had been effected, 2 cc. of sodium cobaltinitrite prepared according to the directions of de Koninck (6) was added. In order to insure complete precipitation the mixture was allowed to stand overnight. The precipitate of sodium potassium cobaltinitrite was collected in a glass filtering crucible and washed successively with small portions of 70 per cent alcohol, 95 per cent alcohol and ether, and finally dried at room temperature by drawing air through the crucible for a short time. In order to test the reliability of the method as well as to determine the amount of potassium in the precipitate, blanks containing small known amounts of potassium in the presence of the same amounts of pure potassium- and ammonium-free calcium chloride as were present in the actual determination were run in the way just described. The results will be found in table 2. It is to be noted that potassium in the blanks was present as the chloride. In the table, however, the amount of potassium added, and found, is expressed in terms of the oxalate, the form in which potassium occurs in the contaminated calcium oxalate. The second column of the table gives the value of the experimentally determined factor:

TABLE 2

POTASSIUM OXALATE TAKEN	VALUE OF THE FACTOR $\frac{K_2C_2O_4}{\text{Wt of ppt}}$	POTASSIUM OXALATE FOUND (Factor = 0 20)	ERROR
mg		*mg*	*mg*
0 20	0 18	0 22	+0 02
0 40	0 18	0 44	+0 04
0 70	0 24	0 58	−0 12
1 2	0 23	1 04	−0.18
2 0	0 20	1 98	−0 02

$$\frac{K_2C_2O_4}{\text{Weight of precipitate}}$$

The values obtained are not constant, which is to be attributed in part, at least, to the experimental errors necessarily associated with the handling and weighing of such small quantities of precipitate as are being dealt with here. The value of the factor adopted for use in the calculations is 0.20. The third column of table 2 gives the amount of potassium oxalate found using the factor 0.20; the agreement between the amount taken and that found is quite satisfactory for our purpose.

Ammonium. The ammonium content of calcium oxalate was determined colorimetrically with Nessler's reagent.[2] The washed precipitate of calcium oxalate was dissolved by warming with 2 cc. of concentrated hydrochloric acid diluted with a small volume of water. When all the calcium oxalate had dissolved, the liquid was cooled and diluted with approximately 75 cc. of water. To this solution was added 5 cc. of 6 *N* sodium carbonate in small portions with agitation. Finally, the volume was made up to exactly 100 cc. and after mixing, the liquid was filtered through a glass crucible. Ten cc. of the filtrate was taken and treated in a small vial of 20 cc. capacity with 0.5 cc. of sodium tartrate (50 grams in 100 cc. of water) and 0.5 cc. of Nessler's reagent. The color comparison was made with a series of standards in identical vials made up fresh and treated with sodium carbonate and Nessler's reagent simultaneously with the unknown. The standards usually differed by 0.002 mg. of ammonia. The color comparison was made a few minutes after mixing with Nessler's reagent. On standing, the unknown solution slowly became turbid, but the color comparison could be made quite leisurely without interference from this cause. The presence of tartrate is indispensable; in its absence the unknown becomes turbid so rapidly that the colorimetric determination is rendered impossible. Blanks run with ammonium-free calcium oxalate in the manner described gave satisfactory results, e.g., 0.06, 0.10 and 0.16 mg. of ammonium, respectively, were taken, and 0.06–0.07, 0.10–0.11, and 0.16 mg. were found.

Explanation of tables 3, 4, and 5: coprecipitation of alkalies

The solutions of calcium chloride and alkali oxalate used in these precipitations were all 0.25 *N*. In the ordinary precipitations, the salt in excess was contained in the precipitating vessel and the other solution was added to it with hand shaking until the excess of the first solution was 20 per cent. The volume of water originally added was such that after the precipitation had been made the total volume amounted to 100 cc. in each case. Filtration was made immediately after precipitation; in those cases in which the precipitate was formed in the cold, the filtration and washing required several hours on account of the very finely divided condition of the precipitate. Precipitates obtained in the cold were washed ten times with small portions of cold water, and those formed in hot solution a like number of times with hot water. Precipitation according to Hahn has already been described (7). For the crystal size of the various precipitates see table 2 of a previous paper (7). The amount of alkali oxalate coprecipitated is expressed in two ways in table 3: (1) as milligrams of anhydrous alkali oxalate per gram of calcium oxalate monohydrate, and (2) as millimoles of alkali oxalate per gram of calcium oxalate monohydrate. The alkalies are actually coprecipitated as the oxalates, as is proved by the fact that calcium oxalate precipitated in the presence of much alkali chloride contains merest traces of chloride. In table 4 the results of a systematic study of the coprecipitation of sodium present in the solution as sodium chloride, using ammonium oxalate as precipitating reagent, are reported. In table 5 some results on the coprecipitation of alkalies under conditions similar to those of the ordinary analytical practice are given

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[2] Nessler's reagent: 3.5 grams of mercuric iodide, 25 grams of potassium iodide, and 15 grams of potassium hydroxide in 100 cc. of solution.

TABLE 3

Coprecipitation of alkali oxalates with calcium oxalate

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	EXCESS ION DURING PRECIPITATION	AMOUNT OF ALKALI OXALATE COPRECIPITATED PER GRAM OF CALCIUM OXALATE MONOHYDRATE					
			Sodium oxalate		Potassium oxalate		Ammonium oxalate	
			mg	*millimoles*	*mg*	*millimoles*	*mg*	*millimoles*
1	20 Ox to 24 Ca*, 55 H_2O; R.T.; 1 minute	Ca	24	0.18	19	0.115	5.5	0.044
2	20 Ca to 24 Ox, 55 H_2O; R.T.; 1 minute	Ox	18	0.135	14	0.085	8.0	0.064
3	As in 1, but at 100°C.	Ca	5.0	0.037	0.8	0.0051	0.8	0.0064
4	As in 2, but at 100°C.	Ox	8.5	0.064	1.2	0.0072	1.05	0.0083
5	Hahn's procedure. 21 Ca and 20 Ox; R.T.; 10 minutes	Ca	5.5	0.041	1.0	0.006	0.55	0.0044
6	Hahn's procedure. 20 Ca and 21 Ox; R.T.; 10 minutes	Ox	9.5	0.071	1.4	0.0085	1.15	0.0091
7	As in 5, but at 100°C.	Ca	5.0	0.037	0.5	0.0030	0.1	0.0008
8	As in 6, but at 100°C.	Ox	7.5	0.056	0.55	0.0033	0.1	0.0008
9	As in 2, but digested at 90–100°C. for 18 hours	Ox	See table 4		0.4	0.0024	0.2	0.0016
10	As in 4, but in the presence of 1 g of NaCl	Ox			0.45	0.0027		

* 20 Ox = 20 cc. of 0.25 *N* alkali oxalate; 20 Ca = 20 cc. of 0.25 *N* calcium chloride; R.T. = room temperature.

DISCUSSION OF RESULTS

1. The coprecipitation of sodium is much greater than that of potassium and ammonium no matter what the conditions of precipitation are; the difference is most marked in hot solution, especially if the precipitation is made according to Hahn. The coprecipitation of sodium is then still

TABLE 4

Coprecipitation of sodium present as chloride

PRECIPITATE NUMBER	AMMONIUM OXALATE	CALCIUM CHLORIDE	EXCESS ION DURING PRECIPITATION AND AFTER	WATER	SODIUM CHLORIDE ADDED	TEMPERATURE DURING PRECIPITATION	REMARKS	$Na_2C_2O_4$ COPRECIPITATED PER GRAM OF CaC_2O_4 H_2O
	cc	*cc.*		*cc.*	*moles*	*degrees C.*		*mg.*
1	20	24	Ca	55	0 05	R.T.		31.4
2	24	20	Ox	55	0.05	R.T.		34 0
3	20	24	Ca	55	0 10	100		12 7
4	20	24	Ca	55	0 05	100		9 9
5	20	24	Ca	55	0 01	100		5 9
6	24	20	Ox	55	0 10	100		19 7
7	24	20	Ox	55	0 01	100		9.7
8	As 7; stood five days before filtration							8.2
9	50	20	Ox	30	0 01	100		8.8
10	As 5, but in ammoniacal medium (2 cc. of concd NH_3)							5 5
11	As 7, but in ammoniacal medium (2 cc. of concd. NH_3)							9.95
12	20	24	Ca	55	0 01	R.T.	Acid*	8 1
13	24	20	Ox	55	0 01	R.T.	Acid*	9 6
14	20	24	Ca	55	0 01	100	Acid*	5 5
15	24	20	Ox	55	0 01	100	Acid*	5 5
16	20	21	Ca	55	0 01	R.T.	Hahn's procedure	11 5
17	21	20	Ox	55	0 01	R.T.	Hahn	18 0
18	20	21	Ca	55	0 01	100	Hahn	9 0
19	21	20	Ox	55	0 01	100	Hahn	9 2
20	As 5, but in presence of 5 cc. of glacial acetic acid							4 45
21	As 7, but in presence of 5 cc. of glacial acetic acid							11 5
22	As 21; digested at 100°C. for 18 hours							8 7
23	24	20	Ox	50	0 01	R.T.	5 cc. of glacial acetic acid	18 2
24	As 23; digested at 100°C. for 18 hours							4 75
25	20	24	Ca	55	0 01	R.T.	Digested 18 hours at 100°C.	0 7
26	20	24	Ca	55	0 01	100	Digested 18 hours at 100°C.	1 1
27	As in 26							1 5
28	24	20	Ox	55	0 01	R T.	Digested 15 hours at 100°C.	0 77
29	As in 28							0 82
30	24	20	Ox	55	0 01	100	Digested 18 hours at 100°C.	4 6
31	50	20	Ox	55	0 01	100	Digested 18 hours at 100°C.	0 9
32	20	24	Ca	50	0 01	90	Acid†	3 0
33	24	20	Ox	50	0 01	90	Acid†	3 7

* 2 cc. of concentrated HCl was added to volume of 100 cc., neutralized at R.T. with dilute ammonia (2 minutes).

† 5 cc. of concentrated HCl was added to volume of 100 cc., heated with 3 to 4 grams of urea at 90°C. for 20 hours.

TABLE 5

Coprecipitation of alkalies under analytical conditions

20 cc. of 0.25 N calcium chloride used in all experiments

PRECIPITATE NUMBER	CONDITIONS	$Na_2C_2O_4$ PER GRAM OF $CaC_2O_4 \cdot H_2O$
	A. Sodium	
		mg.
1	30 cc. of 1 molar sodium chloride present. Precipitation made at 100°C. by adding 1 g. of ammonium oxalate in 50 cc. of water to 250 cc. of solution containing 5 cc. of concentrated hydrochloric acid; then neutralized with 4 N ammonia added dropwise	13.0
2	30 cc. of 1 molar sodium chloride present. One gram of ammonium oxalate in 50 cc. of water added to 250 cc. of calcium solution at 100°C., containing 1.0 cc. of concentrated ammonium hydroxide. Time, 1 minute.	8 2
3	30 cc. of 1 molar sodium chloride present. One gram of ammonium oxalate in 25 cc. of cold water added all at once to calcium solution having total volume of 250 cc. Precipitation made at room temperature. Then digested at 100°C. for two days.	2 0
	B. Potassium	
4	0.020 mole of potassium chloride present. Precipitation made at 100°C. by adding 1 g. of ammonium oxalate to 200 cc. of solution containing 2 cc. of concentrated hydrochloric acid and neutralizing with dilute ammonia added dropwise.	1 4
5	0 020 mole of potassium chloride present. Precipitation made at 100°C. by adding rapidly dropwise 1 g. of ammonium oxalate in 50 cc. of hot water to 200 cc. of solution containing 1 cc. of concentrated ammonia.	0 3
	C. Ammonium	
6	One gram of ammonium oxalate in 50 cc. of water added to boiling calcium solution having a volume of 200 cc. Two cc. of concentrated hydrochloric acid present. Then neutralized with dilute (2 N) ammonia added dropwise.	2.4
7	Precipitation made by adding 1 g. of ammonium oxalate in 50 cc. of water to 200 cc. of hot calcium solution containing 1 cc. of concentrated ammonium hydroxide.	2.4
8	Exactly as in 1 except that 1.0 g. of ammonium chloride was present.	3.5

strong (0.5–1 per cent), while that of the other alkalies has decreased to less than 0.1 per cent and sometimes to only 0.01 per cent.

At room temperature—ordinary precipitation—more potassium is coprecipitated than ammonium, but at 100°C. the respective amounts are nearly the same, with an apparent tendency for potassium to exceed ammonium. Precipitates obtained according to the method of F. L. Hahn are contaminated equally if they have been formed in cold solution, but in hot solution more potassium is coprecipitated. In general, potassium tends to be coprecipitated to a greater extent than ammonium. *The order of coprecipitation of alkalies is therefore the order of adsorbability.*

2. It is interesting to note that calcium oxalate formed according to Hahn's procedure in hot solution in the presence of sodium contains as much of this element as when the precipitation is made in the ordinary way in hot solution, so that this special method of precipitation possesses no advantages. Hahn's method gives better results with potassium, and especially with ammonium, but since those elements contaminate the oxalate precipitate formed in the cold only to the extent of 0.05–0.1 per cent of the weight of the precipitate, its application is unnecessary.

3. The order and amount of coprecipitation of sodium added as chloride under various conditions (table 4) correspond in general to the results obtained by precipitating sodium oxalate with calcium (table 3). The high sodium coprecipitation obtained here in Hahn's method is due to the special way in which this procedure has been carried out, i.e., calcium and oxalate were added simultaneously to a solution of sodium chloride. The ratio of sodium to calcium or oxalate present at any moment was therefore large and the amount of sodium coprecipitated was consequently large as expected.

Whether calcium oxalate is precipitated in neutral or ammoniacal solution makes no difference in the amount of sodium carried down. Neutralization of a hydrochloric acid solution of calcium oxalate with dilute ammonia at room temperature or at 100°C. gives a precipitate which still contains as much sodium as that obtained by direct precipitation in neutral or ammoniacal medium. The ion in excess—calcium or oxalate—makes hardly any difference if a strongly acid solution is slowly neutralized.

Crystals of calcium oxalate that are very large can be obtained by adding urea to a strongly acid solution of calcium and alkali oxalate and then digesting the mixture (procedure of H. H. Willard); the slow neutralization of the acid gives a slow precipitation of the oxalate with the consequent formation of large crystals. These, however, still contain fairly large amounts—analytically speaking—of sodium, although less than when the precipitation is made in the standard way.

Only one method under most conditions will give calcium oxalate sufficiently free from sodium to allow its use for precise analysis, and that is the method of recrystallization of a finely divided precipitate formed at room temperature. By precipitating calcium oxalate in a volume of 50 to 75 cc. at room temperature and digesting, the fine crystals first precipitated undergo an entire structural change due to transformation of the higher hydrates, and grow at the expense of the finest, with the result that at the end of a day or so the crystals are a few microns in diameter and then contain much less sodium than originally. It is true that such a precipitate filters considerably more slowly than one obtained under the usual conditions of analytical precipitation. However, by the use of glass filtering crucibles such a precipitate can be filtered and washed in approximately half an hour. It seems to us that this method of procedure is far superior to that of double precipitation of calcium oxalate, which would otherwise be necessary if any considerable amount of sodium is present. The application of the results to analytical work will be discussed in a forthcoming paper.

4. When calcium oxalate is precipitated with excess ammonium oxalate (table 4), no other alkali ion being present, under analytical conditions either by neutralizing a hot acid solution with dilute ammonia or by adding ammonium oxalate directly to a faintly ammoniacal solution, then the amount of ammonium oxalate coprecipitated is of the order of a few tenths of a per cent. In the presence of much ammonium chloride this value becomes larger. Thus, precipitation from acid solution by neutralizing with ammonia in the presence of one gram of ammonium chloride gave a contamination of 0.35 per cent. This amount will not be serious in ordinary analytical work, especially since this error will be compensated by a slight solubility loss in washing with water if the determination is to be made volumetrically with permanganate. If the determination is made according to the gravimetric procedure, a coprecipitation of ammonium is, of course, immaterial.

5. In the precipitation of calcium oxalate from cold solutions, a larger coprecipitation of alkalies is found in the presence of an excess of calcium than of oxalate (table 3, experiments 1 and 2), a result in opposition to the rules of coprecipitation. The explanation of this more or less abnormal behavior is relatively simple. In a study of the formation of higher hydrates of calcium oxalate (previous paper (7)) it has been shown that at room temperature fairly large amounts of the higher hydrates are formed. The latter are not stable when left in contact with the mother liquor and are transformed into the monohydrate, this process being completed within twenty-four hours. The higher hydrates are stabilized by an excess of calcium, whereas oxalate ions promote the transformation. This transformation is accompanied by an internal structural change and a recrystallization resulting in a purification of the primary precipitate; this purification takes place much more quickly in a presence of an excess of oxalate

(experiment 2, table 3) than of calcium (experiment 1). The filtration and washing of the precipitates obtained at room temperature is slow, more than two hours being required. The amount of coprecipitated alkali found is, therefore, more or less accidental (see, for example, experiments 1 and 2, table 4, where more sodium was coprecipitated if oxalate was in excess); it may be expected that the primary precipitate formed in the presence of an excess of oxalate will contain more sodium than that separated from a solution containing an excess of calcium. That the above interpretation is correct will be shown in a discussion of the coprecipitation of iodate with calcium oxalate (next paper); and further, in a paper dealing with the internal structural changes on the aging of freshly prepared calcium oxalate, it will be demonstrated that the fresh precipitate formed in the cold is porous and permits fairly rapid effusion of foreign constituents from, or diffusion into, its interior. If no higher hydrates are formed (precipitation according to Hahn; experiments 5 and 6, table 3; 16 and 17, table 4), the coprecipitation of the alkalies is in harmony with the general rules, i.e., more alkali in the precipitate if the oxalate is in excess.

6. In the precipitation of calcium oxalate at higher temperatures invariably more alkali is carried down in the presence of an excess of oxalate than of calcium, a result in harmony with the rules of coprecipitation. The coprecipitation of sodium increases with increasing excess of oxalate in the medium. Since no higher hydrates of calcium oxalate are formed at higher temperature, this normal behavior was anticipated.

7. The amount of coprecipitation of alkalies at 100°C. is much less than at room temperature. At the present time it is impossible to make any predictions regarding the influence of the temperature upon the amount of coprecipitation, since the conditions of crystal growth, the speed of adsorption, and the adsorbability of the ions at the two temperatures are quite different, and no quantitative information is available for a systematic analysis of these factors at different temperatures. It is interesting to note that in contrast to the alkalies, the coprecipitation of the anions is invariably higher at 100°C. than at room temperature (compare with next paper).

8. Coprecipitation of one alkali ion does not prevent the carrying down of another alkali in the same precipitate. Thus it is shown by experiment 10 (table 3) that sodium and potassium are simultaneously coprecipitated, whereas comparison of results of experiments in tables 3 and 5 indicates that ammonium and potassium are carried down at the same time. This result is not surprising, because during the growth of the precipitate competition between the various foreign ions to be adsorbed at the surface of the growing particles takes place and the coprecipitation of the ion with the highest adsorption potential will predominate. A coprecipitation of only one type of ion if other kinds of the same sign are present, as D.

Balarew (8) claims to be the case, is contrary to what we may expect from our knowledge of adsorption and coprecipitation phenomena and to experimental evidence.

9. The coprecipitation of sodium with calcium oxalate does not increase linearly with the concentration of the alkali ion in the solution, but seems to be an exponential function of the latter (compare experiments 3, 4, and 5, table 4). Thus with 0.01 mole of sodium chloride in the solution 5.9 mg. of sodium oxalate were coprecipitated; with 1.0 mole in the same volume, 12.7 mg. of sodium oxalate were coprecipitated. Such an exponential relation may be expected from our knowledge of the relation between amount adsorbed and equilibrium concentration in the solution. Therefore, a relatively large coprecipitation of an ion which is strongly adsorbed may be expected even if it is present in fairly small concentrations.

10. Digestion of a freshly formed precipitate results in a purification of the crystals. The most effective method of obtaining pure calcium oxalate is by precipitation from a weakly acid solution (pH 4 to 6; compare paper V of this series) at room temperature and digestion for eighteen hours or so thereafter.

11. The reproducibility of the coprecipitation experiments is fairly good, if the precipitations are repeated under identical conditions.

SUMMARY

1. The order of the adsorption of alkali ions by, and coprecipitation with, calcium oxalate is the same, sodium being more strongly adsorbed and coprecipitated than potassium and the latter more strongly than ammonium.

2. Ammonium oxalate is less adsorbed and coprecipitated than the potassium salt, a result contrary to the adsorption rule of Paneth-Fajans.

3. The presence of an excess of the lattice ion in the solution decreases, but does not necessarily prevent, the adsorption and coprecipitation of ions of the same sign, foreign to the lattice.

4. The coprecipitation of alkali ions with calcium oxalate is larger if there is an excess of oxalate instead of calcium in the solution during the precipitation. An apparent exception to the coprecipitation rule is found if precipitation takes place from relatively concentrated solutions at room temperature. This abnormal behavior is explained by the fairly rapid transformation of the higher hydrates accompanied by radical structural changes and recrystallization after the precipitation.

5. A study has been made of the coprecipitation of alkali ions under analytical conditions. Sodium, especially, can seriously contaminate the precipitates.

6. By far the purest calcium oxalate is obtained if the precipitation is made at room temperature from relatively concentrated solutions at a

pH of 4 to 6 and the mixture is digested for about twenty hours on the steam bath.

7. The coprecipitation of the alkalies at 100°C. is much smaller than at room temperature.

8. Coprecipitation of one alkali ion does not prevent the carrying down of another alkali in the same precipitate.

9. The amount of sodium and other alkalies coprecipitated is an exponential function of the alkali concentration in the solution. Relatively speaking, there is already a marked coprecipitation in dilute solutions.

REFERENCES

(1) KOLTHOFF, I. M.: J. Phys. Chem. **36**, 860 (1932).
(2) BEEKLEY, J. S., AND TAYLOR, H. S.: J. Phys. Chem. **29**, 942 (1925).
(3) ODÉN, SVEN: Arkiv. Kemi. Mineral. Geol. **7**, No. 26 (1920).
(4) PINKUS, A., AND BROUCKÈRE, L. DE.: J. chim. phys. **25**, 605 (1928).
DE BROUCKÈRE: J. chim. phys. **26**, 250 (1929); **27**, 543 (1930).
(5) BARBER, H. H., AND KOLTHOFF, I. M.: J. Am. Chem. Soc. **50**, 1625 (1928).
(6) DE KONINCK: Z. anal. Chem. **49**, 53 (1910).
(7) SANDELL, E. B., AND KOLTHOFF, I. M.: J. Phys. Chem. **37**, 153 (1933).
(8) Compare BALAREW, D.: Kolloidchem. Beihefte **30**, 249 (1930).

STUDIES IN COPRECIPITATION. V

The Coprecipitation of Anions with Calcium Oxalate

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In this paper the results of an extensive study of the coprecipitation of the iodate ion will be described, and some data will be reported on the carrying down of bromate, chromate, sulfate, and the halides by calcium oxalate. In addition a study has been made of the ratio of calcium to oxalate in precipitates obtained under various conditions. This ratio is found to be smaller than the theoretical one if the calcium oxalate contains occluded oxalate, whereas it is larger than unity if a coprecipitation of calcium salts predominates. This investigation of the calcium-oxalate ratio was made primarily for these two purposes: (a) for studying the coprecipitation of hydroxyl ions (as calcium hydroxide) with calcium oxalate; (b) for finding conditions under which the ratio approaches the theoretical value. The practical significance will be discussed with other data in a forthcoming analytical paper.

I. COPRECIPITATION OF IODATE

Calcium iodate is a sparingly soluble salt and for this reason it may be expected that calcium oxalate precipitated from solutions containing iodate will be contaminated by it appreciably. This is actually found to be the case. The amount of iodate coprecipitated is usually never very large, but since even small amounts can be determined very simply and accurately, the coprecipitation of this ion with calcium oxalate has been studied in a systematic way.

The iodate in the precipitate was determined by transferring the washed calcium oxalate to a flask containing 50 to 100 cc. of water. Pure potassium iodide containing no iodate was then added, and finally hydrochloric acid to dissolve the precipitate and to liberate iodine by reaction of the iodate with the iodide. Hydrochloric acid must not be added before the iodide, for then some of the iodate will react with the oxalate and an insufficient amount of iodine will be liberated upon the subsequent addition of iodide. The liberated iodine was titrated with dilute sodium thiosulfate, usually 0.01 *N*, with starch as indicator. Blanks with pure calcium oxalate and known amounts of iodate gave satisfactory results.

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The results of a systematic series of coprecipitation experiments are given in table 1.

EXPLANATION OF TABLES 1 AND 2

Part A. The calcium chloride solution used was 0.25 *N*, the ammonium oxalate solution 0.50 *N*. Ten cc. of potassium iodate solution containing 0.200 g. of the anhydrous salt were mixed with 24 cc. of calcium chloride solution and 55–65 cc. of water (this particular volume of water was

TABLE 1

Coprecipitation of iodate

A. Ammonium oxalate added to excess calcium chloride

NO	TEMPERATURE	TIME OF PRECIPITATION	CC OF 0 0100 *N* THIOSULFATE			REMARKS
			0 01 *N* HCl	0 05 *N* HCl	Concentrated HCl	
	degrees C	*minutes*				
1	25	1			2 85	12 cc. of ammonium oxalate used instead of 10 cc.
2	25	1			2 85	
3	25	1			1 80	Heated to boiling before filtration
4	25	1			4 3	10 cc. of ammonium oxalate
5	25	1	1 00	—	3 8	
6	25	20	0 20		3 8	
7	25	1		1 45	6 5	50 cc. of calcium chloride
8	25	1		0 55	3 15	Mechanically stirred
9	25	15		0.45	2 3	Mechanically stirred
10	100	1			9 5	
11	100	1	0 35		9 9	
12	100	1		0 6	9 1	Stood 18 hours before filtration
13	100	1		0 55	10 2	
14	25	1	1 05		18 2	25 cc. of alcohol present
15	25	1		0.45	4 80	Precipitated in presence of 25 cc. of alcohol; then boiled 30 minutes before filtration
16	25	1			4 5	0.1 gram of agar present
17	25	1		0 75	7 0	10 cc. of 6 *N* acetic acid present
18	25	1		0 3	17 2	50 cc. of 6 *N* acetic acid present
19	100	1		1 1	13.1	25 cc. of alcohol present
20	100	1			11 0	0.1 gram of agar
21	100	1			12.7	10 cc. of 6 *N* acetic acid present
22	25	1		0.3	4.4	0.40 gram of potassium iodate
23	25	1		0 45	3 1	0.10 gram of potassium iodate
24	25	1		0 15	1 8	0.02 gram of potassium iodate
25	100	1		0.3	7 6	0.10 gram of potassium iodate
26	100	1		0 15	3.4	0.02 gram of potassium iodate

TABLE 1—*Continued*

B. Calcium chloride added to excess ammonium oxalate

NO.	TEMPERATURE	TIME OF PRECIPITATION	CC OF 0.0100 *N* THIOSULFATE		REMARKS
			0.05 *N* HCl	Concentrated HCl	
	degrees C	*minutes*			
1	25	1		2.4	
2	25	1	0.7	3.0	Mechanically stirred
3	25	10		2.5	Mechanically stirred
4	25	10	0.2	0.8	Mechanically stirred; 20 cc. of ammonium oxalate
5	25	1		2.9	Hand-shaken; boiled 5 minutes after precipitation
6	25	1	0.10	1.10	Stood 18 hours before filtration
7	25	1	0.15	1.5	Stood 13 days before filtration
8	100	1		6.1	
9	100	1	0.4	5.2	Stood 18 hours before filtration
10	100	1	0.5	6.55	Mechanically stirred
11	25	1	0.45	3.9	25 cc. of alcohol present
12	100	1	0.65	7.3	25 cc. of alcohol present
13	25	5	0.45	2.95	Calcium sprayed into solution with atomizer
14	25	5	0.5	1.6	Calcium sprayed into solution with atomizer; 20 cc. of oxalate
15	100	5	0.4	5.45	Calcium sprayed into solution

C. Precipitation according to F. L. Hahn

NO.	TEMPERATURE	TIME OF PRECIPITATION	ION IN EXCESS	CC OF 0.0100 *N* THIOSULFATE			REMARKS
				0.01 *N* HCl	0.05 *N* HCl	Concentrated HCl	
	degrees C	*minutes*					
1	25	22	Ca	0.4		19.9	
2	25	10	Ca		1.7	25.6	Mechanically stirred
3	25	15	Ca	0.65		16.6	Iodate was dissolved in oxalate, not in water in beaker
4	25	10	Ca		2.1	19.7	Only 0.10 gram of potassium iodate present; stirred mechanically
5	25	20	Ox	0.4		13.5	
6	25	10	Ca		3.9	49.3	50 cc. of 6 *N* acetic acid present; mechanically stirred
7	25	10	Ca		1.9	15.9	20 cc. of alcohol
8	25	10	Ca		1.7	14.0	20 cc. of acetone
9	25	10	Ca		2.8	30.3	Volume 300 cc.; 0.6 gram o potassium iodate present
10	100	20	Ca	0.15		12.90	
11	100	20	Ox	0.10		3.70	
12	100	10	Ca		1.7	34.8	50 cc. of 6 *N* acetic acid; stirred mechanically

chosen in order that the total volume of the solution after precipitation would be practically 100 cc.). To the resulting solution, 10 cc. of ammonium oxalate solution were added over the period of time indicated in the table, usually one minute. The mixture was shaken by hand except where noted. Deviations from this procedure will be found noted in the table under the heading "Remarks." Filtration was begun immediately after precipitation; the precipitate was washed with small portions of hot water, usually five to six in number. It should be mentioned that filter paper was used in this series of experiments for collecting the precipitate. After washing, the precipitate together with the filter paper was transferred to a flask, covered with a little water containing potassium iodide and then enough dilute hydrochloric acid added to make the acid concentration approximately 0.01 *N*. This treatment resulted in the liberation of a little iodine from the iodate present at the surface of the precipitate, which was then titrated with sodium thiosulfate (0.01 *N*). The greater amount of the precipitate still remained undissolved. Concentrated hydrochloric acid was next added to dissolve all the precipitate, and the iodine liberated again titrated. The volume of thiosulfate recorded under "concentrated HCl" in the table is the sum of all thiosulfate required in the titration. The object of this particular mode of procedure was to prove that most of the iodate existed in the interior of the crystal and that it was not mainly adsorbed on the external surface. The preliminary shaking of the precipitate with 0.01 *N* hydrochloric acid and iodide removes whatever iodate may be adsorbed and also dissolves the outer portions of the crystal, thus releasing some of the truly coprecipitated iodate, but the bulk of the crystal remains intact. The length of time that the precipitate was allowed to remain in contact with the dilute acid was usually one or two minutes. In some cases 0.05 *N* hydrochloric acid was used instead of 0.01 *N*.

Part B. The same solutions were used as in Part A and the precipitations made as before except that here the addition of reagents was made in the reverse way, i.e., calcium chloride was added to excess ammonium oxalate containing 0.200 g. of potassium iodate. The final excess of ammonium oxalate was 20 per cent except where otherwise noted.

Part C (Precipitation from extremely dilute solutions—F. L. Hahn's procedure). The solutions of calcium chloride and ammonium oxalate used were both 0.25 *N*. These were added simultaneously from respective burets to 60 cc. of water in which was dissolved 0.200 g. of potassium iodate. Either the calcium or the oxalate solution was kept approximately 1 cc. in excess during the entire addition. At the end of the precipitation 20 cc. of one solution, and 21 cc. of the other had been added. The liquid was stirred by hand unless otherwise stated. In one case (experiment 3) the iodate was dissolved in the ammonium oxalate solution and not in the water to which calcium and oxalate were added.

In the experiments reported in table 2 the precipitations were made in the various ways already described, but after precipitation the calcium oxalate was digested at 90°C. in contact with the solution from which it had been precipitated.

TABLE 2

Effect of digestion upon amount of coprecipitated iodate

NO.	CONDITION OF PRECIPITATION	CONDITIONS OF DIGESTION	CRYSTAL SIZE AFTER DIGESTION	CC. OF 0.0100 N THIOSULFATE		
				0.01 N HCl	0.05 N HCl	Concentrated HCl
			microns			
1	R. T.; calcium and oxalate in equivalent amounts	3½ hours at 95°C.	ca. 2			2.2
2	R. T.; 4 cc. of 0.25 N calcium in excess	18 hours at 85°C.	ca. 2			1.6
3	Same as 2	40 hours at 85°C.	2			1.35
4	Calcium solution evaporated to dryness and then precipitated with oxalate containing iodate; calcium in excess	68 hours at 90°C.	0.5–2	0.00	0.10	0.70
5	Calcium solution evaporated to dryness; treated with 10 cc. of oxalate containing iodate	Diluted to 100 cc. and digested 18 hours at 85°C.		0.05		1.45
6	6 cc. of 1 M calcium chloride precipitated with 10 cc. of 0.50 N oxalate at 100°C.	Total volume of mixture 100 cc.; digested 17 hours at 85°C.	1–2			1.4
7	100°C.; calcium in excess (4 cc. of 0.25 N)	18 hours at 85°C.	1–2			3.0
8	R. T.; 4 cc. of 0.25 N oxalate in excess	66 hours at 90°C.	2			0.2
9	Same as 8	68 hours at 90°C.	2			0.15
10	8 repeated at 100°C.	66 hours at 90°C.	2			0.90
11	2.5 cc. of 1 M calcium precipitated at R. T. with 12 cc. of 0.25 N oxalate	Diluted to 100 cc. after precipitation; 120 hours at 90°C.	Varied from 0.5 to 5	0.0		0.10
12	According to Hahn; oxalate in excess; R. T.	44 hours at 90°C.		0.00	0.90	6.60
13	Ordinary precipitation cold in presence of 25 cc. of alcohol; excess calcium	18 hours at 90°C.	1–2	0.00		0.30

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* R. T. = Room temperature.

The amount of contamination recorded in the tables is the amount found in the weight of precipitate actually worked with, namely, 0.365 g. of calcium oxalate monohydrate.

Table 3 gives in a concise form the amount of iodate coprecipitated under various conditions.

II. COPRECIPITATION OF BROMATE, CHROMATE, AND SULFATE

The results recorded in table 4 were obtained by precipitating under conditions the same as described under iodate. In the case of bromate and chromate 0.0025 mole of the potassium salt was present in the solution from which precipitation took place. The bromate content of the calcium oxalate was determined iodometrically (potassium iodide added first, then hydrochloric acid). Only a few experiments with chromate were made. Chromate in the washed precipitate was determined iodometrically.

TABLE 3

Coprecipitation of iodate

NO	MANNER OF PRECIPITATION	MILLIMOLES OF IODATE COPRECIPITATED PER GRAM OF CALCIUM OXALATE MONOHYDRATE
1	Oxalate added to excess calcium; room temperature	0 017
2	Calcium added to excess oxalate; room temperature	0 011
3	Oxalate added to excess calcium; 100°C.	0 044
4	Calcium added to excess oxalate; 100°C.	0 028
5	Ordinary Hahn method; calcium in excess; room temperature	0 075
6	Modified Hahn method; calcium in excess; room temperature	0 09
7	Modified Hahn method; oxalate in excess; room temperature	0 06
8	Modified Hahn method; calcium in excess; hot solution	0 06
9	Modified Hahn method; oxalate in excess; hot solution	0 017
10	No. 1 digested	0 012
11	No 2 digested	0 001
12	No. 4 digested	0 004
13	No. 7 digested	0 03

The precipitations in the presence of sulfate were made in the same manner as previously described for the other anions. When it was intended to have calcium in excess during the precipitation, 20 cc. of 0.25 N ammonium oxalate were added to 24 cc. of 0.25 N calcium chloride in a volume of 80 cc. in the presence of 0.00100 mole of ammonium sulfate. The volume of the liquid after precipitation was thus 100 cc. When ammonium oxalate was to be in excess, 20 cc. of calcium solution were added to 24 cc. of diluted ammonium oxalate. The particular volume 24 cc. was chosen in order to give an excess of 20 per cent.

The contaminated calcium oxalate, after washing, was dissolved in

TABLE 4

Coprecipitation of bromate, chromate, and sulfate

NO.	CONDITION OF PRECIPITATION	COPRECIPITATED BROMATE	COPRECIPITATED CHROMATE	COPRECIPITATED SULFATE
		Cc of 0.0100 *N* thiosulfate	Cc of 0.0100 *N* thiosulfate	Mg of $CaSO_4$ per gram of $CaOx \cdot H_2O$
1a	Oxalate added to excess calcium; R. T.	0.40	0.80	5.1
1b	As 1a, in presence of 2 grams of ammonium sulfate	0.2		
2a	Oxalate to excess calcium; 100°C.	1.45*	2.0	13.0
2b	As 2a, in presence of 2 grams of ammonium sulfate	0.65		
3	As 1, in presence of 25 cc. of alcohol	1.2	5.7	
4	As 3, repeated at 100°C.	2.0		
5	Calcium added to excess oxalate; R. T.	0.25		2.7
6	As 5, in presence of 25 cc. of alcohol	0.45		
7	As 5, but at 100°C.	—	—	5.3
8	As 2a, stood 1 week at R. T. before filtration	—	—	6.6
9	As 7, stood 1 week at R. T. before filtration	—	—	1.6
10	Hahn's procedure; calcium in excess; R. T.	2.7	1.5	8.8
11	As 10, but at 100°C.	1.5	—	10.0
12	As 10, oxalate in excess	1.5	—	2.9
13	As 11, oxalate in excess	—	—	1.9
14	Hahn's method; calcium in excess; 50 cc. of 6 *N* acetic acid; R. T.; 10 minutes	5.6	—	—
15	As 14, stood 18 hours at R. T. before filtration	4.9	—	—
16	Calcium in excess; acid solution neutralized at R. T. with dilute ammonia	—	—	4.2
17	As 16, but oxalate in excess	—	—	1.9

* As 2a, but with 0.006 mole of $KBrO_3$; coprecipitated 2.7 (cc. of 0.01 *N* thiosulfate).

TABLE 5

Coprecipitation of halides

CONDITION OF PRECIPITATION	MG OF HALIDE PER GRAM OF CALCIUM OXALATE MONOHYDRATE
Oxalate added to excess calcium chloride at 100°C. in presence of 5 grams of sodium chloride	0.12–0.18
Same as 1, except 5 grams of potassium bromide present	0.2
Same as 1, except 5 grams of potassium iodide present	0.3
Hahn's method; calcium chloride in excess; room temperature	0.02
4 repeated at 100°C.	0.02
Oxalate added to excess calcium chloride at room temperature in presence of 35 cc. of alcohol	0.05
Oxalate added to excess calcium chloride at 100°C.	0.1

dilute hydrochloric acid, diluted to 50 cc., heated to boiling, and reprecipitated by neutralizing the acid solution with dilute ammonia. The filtrate from this precipitate, together with the washings, was acidified with hydrochloric acid and one drop of the concentrated acid was added in excess. This solution, containing all the sulfate originally in the calcium oxalate, was treated with 1 cc. of 0.5 *N* barium chloride at 100°C. The barium sulfate was filtered off into a glass filtering crucible after standing overnight. The precipitate was dried at 125°C. and then weighed. Blanks run according to this procedure gave satisfactory results:—calcium sulfate taken, 2.1 and 4.3 mg.; found, 2.1 and 4.5 mg. respectively.

It will be seen that the coprecipitation of calcium sulfate is quite large, especially in hot solution. If calcium is determined gravimetrically by weighing as carbonate, or oxalate (after digestion), the error produced by the presence of sulfate will be small enough to neglect, if the precipitation has been made in the usual manner by neutralizing an acid solution with ammonia; of course, if calcium is weighed as sulfate there will be no error.

III. COPRECIPITATION OF CHLORIDE, BROMIDE, AND IODIDE

The coprecipitation of these ions is so slight that no effort has been made to determine the exact amount. The results in table 5 were obtained by dissolving the washed precipitate in nitric acid, adding silver nitrate, and comparing the turbidity obtained with that produced with known amounts of halides in presence of a like amount of oxalate, nitric acid, and silver nitrate. The chloride content of calcium oxalate is therefore astonishingly small. Even in the presence of large amounts of sodium chloride it does not exceed 0.1 per cent. Bromide and iodide are likewise not carried down in appreciable amounts.

DISCUSSION OF RESULTS

1. All the anions here studied are more strongly coprecipitated under all conditions in the presence of an excess of calcium than of oxalate, a result in agreement with the coprecipitation rule. The effect of the lattice ion in excess is especially striking in the case in which the precipitation is carried out at room temperature in a medium containing about 30 per cent alcohol. In presence of an excess of calcium the amount of iodate coprecipitated corresponds to 18.2 cc. of 0.01 *N* thiosulfate; in presence of an excess of oxalate, the amount corresponds to 3.9. Other anions show an analogous behavior.

Changing the medium by the addition of alcohol or much acetic acid increases the amount of coprecipitation much more at room temperature than at 100°C.

2. Experimentally it has been proved that the coprecipitated ions are in the interior of the crystals and that only a small fraction is externally adsorbed.

3. The amount of coprecipitated iodate increases with the excess of calcium in the solution during precipitation and decreases with the excess of oxalate, a result in agreement with the rules of coprecipitation. A reverse behavior was anticipated and found in the coprecipitation of sodium (preceding paper).

4. The amount of coprecipitated iodate seems to be an exponential function of the iodate content of the solution. With 0.2 g. of potassium iodate in the solution, an amount corresponding to 1.8 cc. of 0.01 *N* thiosulfate is found in the precipitate; with twenty times more iodate in the solution, the coprecipitated quantity increases only 2.5 times (precipitation at room temperature). A similar relation is found if the precipitation is carried out at 100°C.; although the iodate content of the solution was increased five times, the coprecipitated amount increased less than twofold (experiments 25 and 26, table 1, A).

5. The speed of addition of reagent seems to have little if any influence upon the amount of coprecipitated iodate. In experiment 15 (table 1, B) the calcium solution was sprayed into the boiling oxalate–iodate mixture with an atomizer, the solution being mechanically stirred. When the calcium solution was added from a buret, other conditions being the same, and the reacting mixture just shaken by hand, approximately the same amount of iodate was found in the precipitate. If the precipitation is carried out in the ordinary way at room temperature, the amount of coprecipitated iodate seems to decrease slightly with increasing time of precipitation. Here, however, we must remember that the primary precipitate consists of higher hydrates, which are transformed with time into the monohydrate, resulting probably in a release of the coprecipitated iodate. But even at room temperature it was immaterial whether the calcium solution was added in a fine spray from an atomizer or from an ordinary buret (experiments 2, 3, and 13, table 1, B).

6. The maximum amount of anion coprecipitation is found by precipitation at room temperature from extremely dilute solutions (modification of F. L. Hahn's procedure). In spite of smaller crystallization velocity, and consequently the separation of much larger crystals than in the ordinary method, the greatest anion coprecipitation is obtained here. The amount of contamination is particularly large if approximately 25–30 per cent acetic acid is present during the precipitation (experiment 6, table 1, C). In a general discussion of the phenomena of coprecipitation (1) it was predicted that the amount of coprecipitation will increase to a maximum with increasing crystal size, this maximum being reached at a relatively small crystallization velocity. Further decrease of the latter will lead to diminishing coprecipitation. This maximum will not be reached at the same crystallization velocity for various ions, for the speeds of adsorption, adsorbability, and replacement by lattice ions are different for the various ions. From the result of experiment 9 (table 1, C) it is seen that the

amount of coprecipitated iodate increases to a maximum with increasing crystallization velocity. If the latter is still further decreased by working at 100°C., according to Hahn's procedure, the iodate coprecipitation diminishes, although the adsorbability of the iodate ion on calcium oxalate seems to be of the same order at 100°C. as it is at room temperature.

7. In agreement with the results obtained in the study of the alkali coprecipitation, it is found that digestion of the precipitate in the mother liquor before filtration results in a purification of the crystals (see table 2). If the primary precipitate consists of relatively large crystals (2 microns or more), part of the coprecipitated ions are lost by effusion through the capillaries of the crystalline particles. However, no adsorption equilibrium is reached, since most of the contaminant in the interior is no longer in open communication with the outside of the crystals. Again, the most effective method of obtaining pure crystals is precipitation from relatively concentrated weakly acid solutions (pH 4 to 6) at room temperature followed by digestion overnight. The purification is extremely pronounced when about 25 per cent alcohol is present during the precipitation. It was found that a precipitate thus formed at room temperature contained iodate corresponding to 18.2 cc. of 0.01 *N* thiosulfate, and after digestion (experiment 13, table 2) only 0.3 cc.

If the precipitates are allowed to stand in contact with the mother liquor at room temperature before filtration, a distinct purification is noticed if they have been formed at this low temperature from relatively concentrated solutions. This purification process is to be attributed to transformation of the higher hydrates into the monohydrate accompanied by an entire structural rearrangement (compare experiments 1 and 7, table 1, B). Precipitates formed at 100°C. and aged at room temperature undergo little change, these conditions not being favorable for a recrystallization; therefore, no distinct decrease in the amount of iodate coprecipitated is noticed with the time of standing (experiment 12, table 1, A).

8. The coprecipitation of anions decreases in the order: iodate > chromate, sulfate > bromate > chloride, bromide, and iodide. The coprecipitation of the halides is negligibly small under all conditions, but that of sulfate may be of practical significance.

9. The coprecipitation of bromate is decreased by the presence of sulfate (table 4, experiments 1b and 2b), showing again that a coprecipitation of two ions of the same electrical sign may take place simultaneously. A similar result was found in the study of coprecipitation of cations.

10. All the anions here studied show the same behavior of being more strongly coprecipitated from hot solutions than from cold. Exactly the opposite result was obtained in a study of the coprecipitation of alkali ions with calcium oxalate.

11. It is of interest to compare the results of the studies on the copre-

cipitation of cations and anions with calcium oxalate with the postulates of the coprecipitation rules derived theoretically (1).

(a) In agreement with the rules it is found that a greater amount of a foreign cation is carried down by the precipitate if an excess of lattice anion is present during the precipitation, the amount of coprecipitation increasing with the concentration of lattice anion in the solution and diminishing with decreasing concentration of the latter. In the coprecipitation of anions just the reverse behavior is found, entirely in harmony with the rule.

(b) The occlusion of foreign ions is to be attributed to an adsorption during the growth of the crystals; the order of adsorption and coprecipitation is identical.

(c) The amount of foreign material in a precipitate decreases with the time of digestion before filtration. If the primary precipitate consists of very finely divided particles a slow recrystallization takes place, during which adsorption equilibrium is established. In the case of calcium oxalate, the purification is favored by the transformation of higher hydrates into the monohydrate, at least if the primary precipitate was formed at room temperature from relatively concentrated solutions. If the original precipitate is of such size that its solubility approaches that of the macrocrystals, an effusion of part of the impurities through capillaries in the crystals takes place during digestion.

(d) The maximum amount of coprecipitated ions is found at a certain crystallization velocity. No general statements can be made with regard to the location of this maximum, as it may be different for each ion. Since there is no adsorption equilibrium during the growth of the crystals, the crystallization velocity alone, other factors being the same, will not determine the amount of coprecipitation, as the speed of adsorption and desorption, the influence of the temperature on these, the adsorbability of the ions, and the competition between the lattice ions and foreign ions of the same sign to be adsorbed at the surface of the growing particles may be different for each case.

Therefore no general predictions can be made at the present time regarding the influence of temperature upon the coprecipitation. It is striking that all cations studied are less, and the anions more, strongly coprecipitated at higher temperatures than at room temperature.

(e) It should finally be mentioned that the interpretation of the phenomena of coprecipitation with calcium oxalate, if the latter is formed at room temperature from relatively concentrated solutions, is complicated by the fact that higher hydrates are formed, which are more or less readily transformed into the monohydrate. It appears that calcium oxalate is not the most favorable precipitate for a systematic study of coprecipitation phenomena; the investigations will be continued with other substances.

TABLE 6

Oxalate content of calcium oxalate precipitate

NO.	METHOD OF PRECIPITATION	OXALATE CONTENT OF PRECIPITATE WITH RESPECT TO CALCIUM
		per cent
1	40 cc. of ammonium oxalate added to 48 cc. of calcium chloride in a total volume of 160 cc.; room temperature; filtration and washing required several hours	100.76
2	40 cc. of calcium added to 48 cc. of oxalate in a total volume of 160 cc.; R. T.	100.55
3	1 repeated at 100°C.	99 50
4	2 repeated at 100°C.	99 60
5	50 cc. of 0.25 *N* calcium added rapidly dropwise to 350 cc. of solution at 100°C. containing 50 cc. of 0.50 *N* oxalate	100 0
6	Precipitation according to Hahn; 50 cc. of calcium and 49 cc. of oxalate added simultaneously to 200 cc. of water at R. T.; calcium solution kept 1 cc. in excess; time of precipitation, 20 minutes	99 50
7	As in 6, except that oxalate was in excess, i.e , 50 cc. of oxalate and 49 cc. of calcium used	99 95
8	Precipitation according to Hahn in hot solution (100°C. at beginning); calcium solution kept about 2 cc. in excess; total of 51 cc. of calcium and 49 cc. of oxalate used; time, 15 to 20 minutes	99 30
9	8 repeated with oxalate in excess; other conditions precisely the same	99 52
10	Precipitation according to Hahn in acid solution; 49 cc. of calcium and 51 cc. of oxalate added simultaneously to 200 cc. of water at R. T., containing 2.0 cc. of concentrated hydrochloric acid; oxalate was kept 2 cc. in excess; no precipitate appeared until more than 10 cc. of oxalate had been added; time of precipitation, nearly 15 minutes	99 94
11a	Precipitated as in 1, then digested at 100°C. for 24 hours	99 86
11b	Same as 11a	99 71
12	Precipitated as in 8, then digested at 100°C. for 24 hours	99 54 99 73
13	Precipitated as in 3 and then digested at 100°C. for 24 hours	99 58
14	Precipitated as in 4 and then digested at 100°C. for 24 hours	99 73
15	Precipitated as in 1; 20 cc. of 0.10 *N* hydrochloric acid then added and the mixture digested at 100°C. for 24 hours	100 06
16	Precipitated as in 2; 20 cc. of 0.10 *N* hydrochloric acid then added and the mixture digested at 100°C. for 24 hours	100 31
17	Precipitation made as in 1; precipitate was then allowed to stand in solution from which precipitated for 9 weeks	99 66
18	40 cc. of oxalate added to 48 cc. of calcium in 160 cc. of solution containing 1 cc. of 4 *N* acetic acid, at R. T., then digested at 100°C. for 18 hours	100 20

THE OXALATE CONTENT OF CALCIUM OXALATE PRECIPITATES

The results of the investigation of the oxalate content of the calcium oxalate precipitate in which the effect of such factors as temperature, order of precipitation (calcium or oxalate in excess), speed of precipitation, and the like were considered in a systematic way, are given hereunder.

The calcium chloride and ammonium oxalate solutions used were both 0.25 *N*; they were prepared from the best reagents obtainable. Precipitations were made, in general, either by the ordinary method or by that of F. L. Hahn. In the ordinary precipitations, the salt in excess was always contained in the precipitating vessel and the other solution was added to it dropwise from a buret with efficient hand agitation. The excess of calcium or oxalate, as the case required, present finally was 20 per cent. The volume of water originally present was such as to make the final volume 20 cc. By the method of Hahn is meant that mode of precipitation in which calcium and oxalate solutions are slowly added simultaneously from respective burets to water (or some other solution) at such a rate that one of the precipitants is kept about 1 cc. in excess of the other during the whole precipitation. Glass or porcelain filtering crucibles were used exclusively for collecting the precipitate. The precipitate was washed with cold water if the precipitation had been made in the cold, and with hot water if the precipitate had been formed at higher temperatures. Each precipitate was usually washed with ten portions of water of a few cubic centimeters each. The precipitate was divided into two parts after drying: in one, oxalate was determined by titration with tenth-normal potassium permanganate; and in the other, the actual amount of calcium present was found by converting the oxalate to sulfate. Further particulars regarding the precipitations will be found in table 6 which summarizes the results of the systematic study.

DISCUSSION

The interpretation of the preceding results does not present any particular difficulties. Calcium oxalate formed in neutral solution is always contaminated with calcium hydroxide. The oxalate content of a precipitate formed in the cold is larger than 100 per cent, but this is accounted for by the strong coprecipitation of ammonium oxalate at this temperature, which is sufficient in amount to overbalance the deficiency caused by the simultaneous coprecipitation of calcium hydroxide. Such a precipitate on digestion easily loses the occluded ammonium oxalate (see previous paper on coprecipitation of alkalies) but not the calcium hydroxide, which appears to be tenaciously held by calcium oxalate, and therefore the oxalate content of the precipitate falls below the theoretical. A precipitate formed in hot solution shows a deficiency in oxalate before digestion because ammonium oxalate is not carried down to any extent at this temperature; the oxalate content after digestion is sensibly the same as before. The precipitates formed slowly according to the procedure of Hahn also contain hydroxide, but to quite different extents depending upon the manner of precipitation. The contamination is greatest at 100°C. in presence of excess calcium and slightly less with excess oxalate. At room temperature a large coprecipitation occurs in presence of excess calcium, but the composition of the precipitate is nearly the theoretical when oxalate preponderates, just as would be expected. Hahn's precipitate formed in dilute acid solution is found to have the theoretical oxalate content within the limits of experimental error. If a precipitate thrown down at room temperature is digested in the presence of dilute acid, it loses all the hydroxide and gives crystals containing a slight excess of oxalate, probably in the form of oxalic acid. Finally, a precipitate formed at room temperature and allowed to stand in the solution from which precipitated loses ammonium oxalate and shows the same deficiency in oxalate as the digested precipitate (transformation of higher hydrate into monohydrate).

It was found that calcium oxalate tends to be contaminated much more strongly by hydroxide, or basic oxalate, than by acid oxalates or oxalic acid (to be described in an analytical paper). This behavior is readily understandable when it is recollected that calcium hydroxide is sparingly soluble. Hydroxide is so strongly adsorbed by calcium oxalate that recrystallization is not of much avail in producing a pure crystal. The decreasing solubility of calcium hydroxide with rise in temperature may contribute to the failure of the recrystallization method. Digestion in presence of dilute acid, however, removes the hydroxide.

SUMMARY

1. The coprecipitation of anions with calcium oxalate decreases in the order: iodate > chromate, sulfate > bromate > chloride, bromide, iodide. The coprecipitation of the halides under all conditions is negligibly small; that of sulfate may be of practical importance analytically.

2. All anions studied are more strongly coprecipitated in the presence of an excess of calcium than of oxalate, the amounts increasing with the excess of calcium and decreasing with excess of oxalate in the solution.

3. All the anions are more strongly coprecipitated from hot solutions than from cold, a behavior just the reverse of that shown by the cations.

4. It has been shown that a coprecipitation of two anions may take place simultaneously.

5. The amount of coprecipitated iodate is an exponential function of the concentration in the solution during the precipitation.

6. The maximum amount of coprecipitation of iodate has been found at a relatively small crystallization velocity.

7. The speed of addition of reagent seems to be of little influence upon the amount of coprecipitated iodate.

8. Hydroxyl ions are strongly adsorbed by, and coprecipitated with, calcium oxalate. Even on mixing neutral solutions of calcium chloride and alkali oxalate a coprecipitation of calcium hydroxide, to be attributed to a hydrolytic adsorption of hydroxyl ions during the precipitation, is found. The amount of coprecipitated hydroxyl ions increases with increasing alkalinity of the solution and must be considered in the volumetric determination of calcium as oxalate.

9. Coprecipitated hydroxyl ions are not entirely removed by recrystallization, thus showing their strong adsorbability. By precipitation or recrystallization from weakly acid medium all calcium hydroxide is removed.

10. Again it was shown that the purest calcium oxalate is obtained if precipitation is made at room temperature from relatively concentrated, weakly acid (pH 4 to 6) solutions and digested for twenty hours thereafter. The calcium-oxalate ratio in such precipitates approaches within the experimental error the theoretical 100.0:100.0.

11. In a discussion of the results of the coprecipitation of cations and anions with calcium oxalate, it has been shown that good agreement exists between theory and experiment.

REFERENCE

(1) KOLTHOFF, I. M.: J. Phys. Chem. **36**, 860 (1932).

MAGNETIC SUSCEPTIBILITIES OF HYDROCHLORIC ACID AND LITHIUM CHLORIDE SOLUTIONS

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The present paper is a report on some measurements of the magnetic susceptibilities of solutions of hydrochloric acid and lithium chloride over a wide concentration range. It may be stated in advance that in the case of the hydrochloric acid solutions our measurements do not show the maxima and minima in the susceptibility-concentration plot found recently by Farquharson (1). However, with the lithium chloride solutions there appear to be two definite discontinuities in the variation of the susceptibility with concentration.

METHOD AND APPARATUS

The method employed in determining the susceptibility of the solutions was the so-called "cylinder" method of Gouy (2). In this method a small glass tube, half filled with the solution, is suspended vertically from the arm of an analytical balance so that the lower edge of the meniscus is located in the middle of the pole gap of an electromagnet. When the magnetic field is excited there is a change in weight of the tube and its contents, which depends on the difference between the susceptibility of the air in the upper portion of the tube and the susceptibility of the solution. In order to eliminate the action of the magnetic field on the uniform glass tube, the latter was of such a length that both extremities were in a field of negligible intensity.

The essential details of the apparatus used in the present measurements may be summarized briefly. The magnet was one giving a field of about 5000 gauss with a current of 5 amperes passing through the coils. The pole pieces were conically tapered and had faces 2.5 cm. in diameter. The pole gap was kept constant at 1.1 cm. The cylinder which held the solution was a soft glass tube, sealed at one end, 14 cm. long and 7.9 mm. in internal diameter. The balance was an assay balance sensitive to less than 0.02 mg. It was mounted on a platform above the magnet and was unaffected by the field. To the left pan of the balance was attached a silk thread which, passing through an opening in the floor of the balance case, served as a suspension for the cylinder. At the lower end of the thread was attached a small glass plug provided with a thin rubber collar, over which the cylinder could be slipped and held firmly.

The routine of the experimental procedure may be described at this point. To the clean and dry cylinder a measured sample of the solution was transferred by means of a calibrated pipette which delivered 3.428 cc. of water. After the cylinder was attached to the suspension, its position was adjusted so that the lower part of the meniscus was at the center of the pole gap. The weight of the cylinder and the solution was then found with no current passing through the coils. Following this weighing the current was switched on and brought up slowly to 5 amperes. After an interval of one minute, which was allowed for the current and field to become constant, the weight of the cylinder and contents was again determined. When the gain in weight of the tube had been found, the current was cut off and the entire procedure, outlined above, was repeated without changing the contents of the tube. In practically every case a duplicate set of measurements was made with a second filling of the tube, thus yielding altogether four determinations of the change in weight produced by the magnetic field. Both as a check on the apparatus and for use in calculating the susceptibilities of the solutions, the gain in weight of pure water under the conditions just described was determined at frequent intervals during the course of the experiment.

The specific susceptibilities of the solutions were calculated by means of the formula:

$$\chi = \kappa \cdot \frac{w_1}{w_2} \cdot \frac{1}{d}$$

The constant κ is the volume susceptibility of the reference substance, water; w_1 and w_2 are the gains in weight of solution and water, respectively; and d is the density of the solution. The standard of reference (3) for measurements of this type is the mass susceptibility of water at 20°C., -0.720×10^{-6}. Therefore, since all of the present experiments were carried out at a temperature within one-half degree of 29°C., the constant κ has the value -0.717×10^{-6}.

The density d was determined in two ways. With the hydrochloric acid solutions the weight of the "cylinder" was found before as well as after the transfer of the known volume from the carefully calibrated pipette. The densities calculated from these data were found to be sufficiently accurate. The densities of the lithium chloride solutions could not be measured by the foregoing procedure because of the failure of these rather viscous solutions to drain completely. Accordingly they were determined separately in a 10-cc. pycnometer bottle.

PREPARATION OF SOLUTIONS

Three different series (I, II, III) of hydrochloric acid solutions were measured. The solutions of series I were prepared from a stock solution which was the middle third portion of the distillate obtained from approximately 6 *M* acid. The stock solution II was the last quarter fraction of a similar distillation. The distillation apparatus in both cases consisted of a Pyrex, glass-stoppered distilling flask over the side arm of which was slipped a quartz condenser. The distillate was collected in a Pyrex bottle, and therefore came in contact only with Pyrex or quartz. Duplicate gravimetric analyses of each of these stock solutions checked to within at least one part in five thousand and showed them to be very close to the constant boiling acid in strength. The various dilute solutions prepared from these two stock solutions were made by adding to a weighed quantity of the latter best thrice-distilled water. The weight of the resulting solution was then found and from these data the percentage composition of the diluted solution was calculated. The more concentrated hydrochloric acid solutions (III) were prepared by slowly passing dried hydrogen chloride gas from an all Pyrex generator directly into a weighing flask containing a weighed amount of water. The flask and contents were cooled with ice water during the absorption. The amount of hydrogen chloride gas absorbed was found from the gain in weight.

Two different series of lithium chloride solutions were measured. The lithium chloride used in preparing stock solution I was purified as follows: C. P. lithium chloride was dissolved in best water, filtered, and precipitated with ammonium carbonate. The resulting lithium carbonate was washed by decantation ten times with distilled water and eight times with hot distilled water to remove ammonia ion and contaminating alkaline carbonates. After drying, this purified carbonate was almost completely dissolved in best distilled hydrochloric acid. The resulting chloride was filtered to remove the residual carbonate and then evaporated in a quartz dish until crystals of lithium chloride appeared. The minimum amount of water required to dissolve the crystals was added and the resulting solution stored in glass-stoppered Pyrex bottles. Analysis of this stock solution showed it to be practically saturated. The various solutions of series II were prepared by Mr. R. W. Wilson for another experiment and were generously placed at our disposal. The purification of the lithium chloride in this case differed from that described above in only one essential. The chloride obtained by conversion of the carbonate was carefully crystallized. The crystals were washed and separated from the mother liquor by an efficient centrifugal process.

RESULTS

In table 1 are tabulated the experimental data bearing on the hydrochloric acid solutions. The number in the first column indicates the stock

TABLE 1

Specific susceptibility of hydrochloric acid solutions

SOLUTION SERIES	HYDROCHLORIC ACID	$-\chi \times 10^6$
	per cent	
II	6 54	0 712
II	9 15	0 710
I	15 00	0 704
I	15 48	0 702
I	15 95	0 702
I	16 48	0 700
I	16 83	0 700
I	17 36	0 701
I	17 81	0 699
I	18 20	0 698
II	18 53	0 700
I	18 66	0 694
I	19 28	0 698
I	19 81	0 696
II	20 19	0 696
III	26 45	0 688
III	27 27	0 688

TABLE 2

Specific susceptibility of lithium chloride solutions

SOLUTION SERIES	LITHIUM CHLORIDE	$-\chi \times 10^6$
	per cent	
II	4 12	0 716
II	9 66	0 712
I	11 02	0 710
I	13 88	0 708
II	16 28	0 707
I	17 08	0 706
I	17 97	0 705
I	18 74	0 704
II	18 97	0 705
I	19 75	0 703
I	20 85	0 699
I	22 59	0 696
II	26 02	0 689
I	32 80	0 679
II	34 90	0 678
II	42 08	0 669
I	44 49	0 665

from which each solution was prepared. The second and third columns give respectively the percentage concentration of the solutions and the calculated specific susceptibility. Table 2 contains the corresponding data for lithium chloride. It may be noted that these tables include results for all the solutions which were prepared.

In practically every case the figure given for the specific susceptibility is the mean result of at least four measurements of the gain in weight of the cylinder and solution, two each being made with separate fillings of the cylinder. The average deviation of the individual remeasurements amounts to less than 0.5 per cent. The latter figure is slightly less than the estimated precision of the least precise measurement, which was the determination of the change in weight. Since the sensitivity of the balance was 0.02 mg. and since the gain in weight was about 4 mg., the precision of this measurement would be approximately 0.5 per cent.

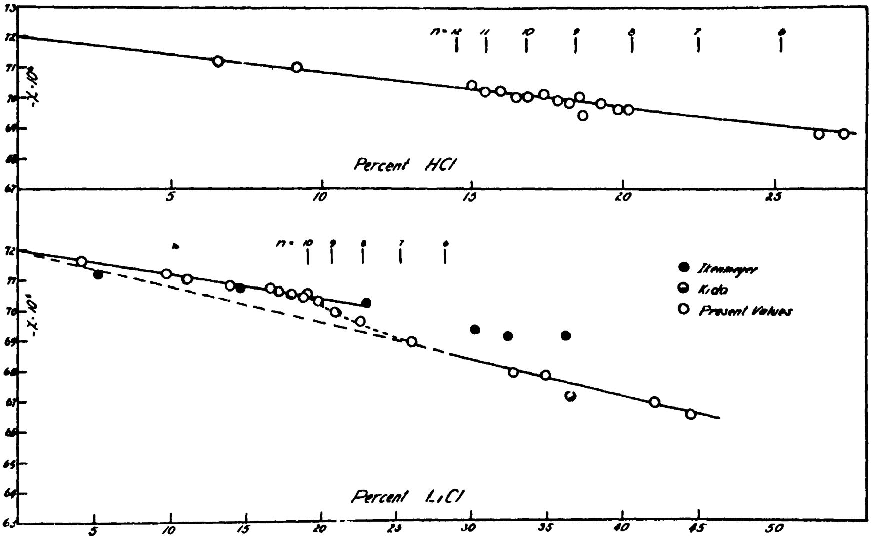

FIG. 1. THE SUSCEPTIBILITY-CONCENTRATION PLOTS FOR HYDROCHLORIC ACID AND LITHIUM CHLORIDE SOLUTIONS

DISCUSSION

The variation of the observed specific susceptibilities of the hydrochloric acid solutions with percentage concentration (figure 1) is linear within the limits of the experimental error, thus indicating that the susceptibilities of the solute and solvent are additive throughout the given range of concentration. If the drawn line is taken to represent the variation of the susceptibility with concentration, the specific and molar susceptibilities of hydrochloric acid are calculated to be -0.602×10^{-6} and -22.0×10^{-6}, respectively. These figures are identical with those obtained by Hocart (4) who, using the "ascension" method, claimed a precision of 0.1 per cent.

The present results are not in agreement with the recent measurements of Farquharson (1) by a different method. The susceptibility-concentration curve obtained by this investigator exhibits well-defined maxima and minima which occur in most cases at concentrations corresponding to stoichiometrical hydrates. A majority of the solutions measured in the present experiment fall within the concentration range ($HCl + 8H_2O$ to $HCl + 12H_2O$) where Farquharson found the greatest variation but, as can be seen in figure 1, there is no significant indication of the fluctuations to be expected. No explanation of the divergent results can be offered at this time.

The susceptibility-concentration data of the lithium chloride solutions (table 2) are also shown graphically in figure 1. It is at once evident that the variation of the susceptibility with concentration is not uniform over the entire concentration range. Before considering the possible significance of this irregularity it should be noted that Ikenmeyer (5), the only other investigator to have measured a series of lithium chloride solutions, found the variation to be quite normal. Since the two sets of measurements deviate[1] seriously only in the more concentrated solutions, it is of interest to observe that a recent single measurement by Kido (6) is in better agreement with present values than with those of Ikenmeyer.

A closer inspection of figure 1 shows that the variation of the susceptibilities of lithium chloride solutions with concentration is linear over two limited concentration ranges: 0 per cent to 19 per cent and from 28 per cent to the saturated state, 44.5 per cent. While the susceptibilities of the salt and water may therefore be treated as additive within the given limits, the susceptibility of the lithium chloride is clearly different in the two cases. Its two values, computed on the basis of the drawn lines, are:

	0 to 19 per cent lithium chloride	*28 to 44 per cent lithium chloride*
χ =	-0.637×10^{-6}	-0.598×10^{-6}
χ_m =	-27.0	-25.4

If this analysis of the data is correct, the non-linear variation of susceptibility with concentration in the intermediate concentrations range, 19 per cent to 28 per cent, must be attributed to the inconstancy of the susceptibility of the salt solute.

A clue to the cause of the assumed change in the susceptibility of the dissolved lithium chloride is to be found in the fact that the 19 per cent solution, which marks the upper concentration limit of one susceptibility value, has the composition $LiCl + 10H_2O$. The concentration limit of the other susceptibility value is not so sharply defined but, from the variation of the susceptibility of the solute with the number of moles of water, it seems to be the solution (28.2 per cent) with the composition $LiCl + 6H_2O$. This connection between the changes in the susceptibility of the solute and the stoichiometrical composition of the solutions suggests immediately that the changes result from an alteration in the degree of hydration of one of the ions in solution. Although hydration is doubtless a factor, it is probably not the only one. For, according to theoretical considerations of Weiss (7), the loss of water of hydration should result in an increase rather than the observed decrease in the apparent magnetism of the solute. However, if as a consequence of the loss of water of hydration the non-hydrated ions become associated to form ion-pairs or clusters (8), the argument of Weiss would require a diminution of the diamagnetic susceptibility of the chloride ion. Since this last factor is conceivably greater than the hydration factor in its effect on the susceptibility, the observed alteration in the diamagnetic susceptibility of the lithium chloride may be the net result of two different changes occurring in the solution state.

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[1] In view of this disagreement it may be mentioned that Reicheneder (Ann. Physik. [5] **3**, 58 (1929)), who subsequently employed Ikenmeyer's method to measure the susceptibilities of solutions of halogen acids, cricitized the method and concluded that it was definitely unsuited for precision measurements.

Whatever the factors are that cause the susceptibility of lithium chloride to undergo a change with concentration, they may reasonably be expected to affect other physical properties of these solutions. Despite the fact that the evidence bearing on this conclusion is very fragmentary and in part conflicting, it does show that the concentrated solutions of lithium chloride are to be regarded as abnormal. A few cases of particular interest may be considered. Hüttig and Keller (9) measured the densities, refractive indices, and the absorption of solutions of the lithium halides at 20°C. The curves obtained by plotting the first two of these properties and coefficient of extinction against the number (n) of moles of water per mole of salt showed discontinuities when $n = 6$, near 30, and 75. Subsequent measurements (10) of the refractive indices of lithium chloride solutions at a number of different temperatures do not indicate, apparently, the discontinuities found by Hüttig and Keller. Further, from the variation with concentration of the apparent molal volume of lithium chloride in solution (11) it is clear that the variation of the density of these solutions with concentration undergoes an abrupt change at the same concentration observed in the susceptibility measurements, namely, $n = 10$. Moreover, since the densities of the more concentrated solutions are larger than those which would follow from the variation of this property in dilute solutions, it may be supposed that the change in the solution state above the critical concentration is not simply the breakdown of a "chemical" hydrate. Whether there is another discontinuity at $n = 6$ cannot be ascertained from the available data. While the apparent molal volume method gives a result different from that obtained by the less sensitive method of Hüttig and Keller, it does confirm their conclusion in the case of lithium bromide and possibly lithium iodide solutions that the density-concentration variation has a discontinuity at the concentration $n = 6$. Finally, in support of the supposition that in the concentrated solutions of lithium chloride the ions are in partial contact as ion-pairs an experiment by Blair and Schofield (12) may be mentioned. According to these investigators the flow-pressure curve of an almost saturated solution of lithium chloride is decidedly anomalous. Their results they interpret to mean that "small strains are not dissipated immediately during the flow, which may well be due to the persistent tendency of the ions to maintain a non-random distribution."

In conclusion the writers wish to acknowledge the generous advice and assistance which they have received from Professor Claude W. Heaps.

REFERENCES

(1) FARQUHARSON: Phil. Mag. **12**, 283 (1931).
(2) GUOY: Compt. rend. **109**, 935 (1889).
(3) INTERNATIONAL CRITICAL TABLES, Volume VI, page 356.
(4) HOCART: Compt. rend. **188**, 1151 (1929).
(5) IKENMEYER: Ann. Physik [5] **1**, 169 (1929).
(6) KIDO: Science Repts. Tôhoku Imp. Univ. **21**, 149 (1932).
(7) WEISS: J. phys. radium **1**, 185 (1930).
(8) FAJANS: Trans. Faraday Soc. **23**, 357 (1927).
(9) HÜTTIG AND KELLER: Z. Elektrochem. **31**, 390 (1925).
(10) KOHNER: Z. physik. Chem. **B1**, 427 (1928).
FONTELL: Soc. Sci. Fennica Commentationes Phys. Math. **4**, 8 (1927).
(11) MASSON: Phil. Mag. [7] **8**, 218 (1929).
SCOTT: J. Phys. Chem. **35**, 2315, 3379 (1931).
GEFFCKEN: Z. physik. Chem. **155**, 1 (1931).
(12) BLAIR AND SCHOFIELD: Phil Mag. [7] **11**, 890 (1931).

THE OXIDES AND HYDRATES OF ALUMINUM

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The oxides and hydrates of aluminum have been the subject of many investigations because of their commercial importance and scientific interest. The apparent multiplicity of forms in which they occur, however, has led to much confusion in their identification. A recent contribution from Weiser and Milligan (1) is indicative of this situation. After reviewing part of the literature and describing their experimental work, they reach the conclusion that there is only one crystalline monohydrate of aluminum, namely, diaspore. The form which a number of other workers have characterized as monohydrate and an isomer of diaspore, they decide is either a new form of alumina, which they call delta-alumina, or perhaps a hemihydrate. This conclusion seems likely to be untenable, once all the facts are considered.

Probably Weiser and Milligan were unaware of the contribution on this subject published in "The Aluminum Industry—Aluminum and its Production" (2). The various forms of oxides and hydrates are there described with information regarding the monohydrates and methods of producing one of them. A brief review of these forms will be given before presenting additional evidence for the existence of the two forms of monohydrate.

ALUMINA

Corundum is the naturally occurring form of alumina,—Al_2O_3, or alpha-alumina, as it is commonly designated. Alpha-alumina is formed by heating any of the hydrates of aluminum to a sufficiently high temperature and is also the form commonly taken by fused alumina upon solidification.

Alumina may be produced in another form known as beta-alumina, by fusing alumina with small amounts of magnesia or sodium carbonate.

A third crystalline form of alumina, which is of considerable interest, is designated gamma-alumina. When aluminum monohydrate or trihydrate is dehydrated by heating, the product first formed is amorphous. With continued heating at higher temperatures of about 500°C., a new crystalline phase begins to appear, which has been identified by its x-ray pattern and named gamma-alumina. Continued heating at higher temperatures—above about 1200°C.—results in its conversion into alpha-alumina.

A fourth crystalline form of alumina has been reported by Barlett and designated as zeta-alumina (3).

ALUMINUM HYDRATES

There are two well-recognized and identifiable hydrates of aluminum, namely, the trihydrate and the monohydrate, and two crystal forms of each.

Aluminum trihydrate occurs in nature as the mineral gibbsite, which is found also in many types of bauxites. This hydrate, designated alpha-trihydrate (α-$Al_2O_3 \cdot 3H_2O$), is the product produced by auto-precipitation from sodium aluminate solutions, as in the Bayer process.

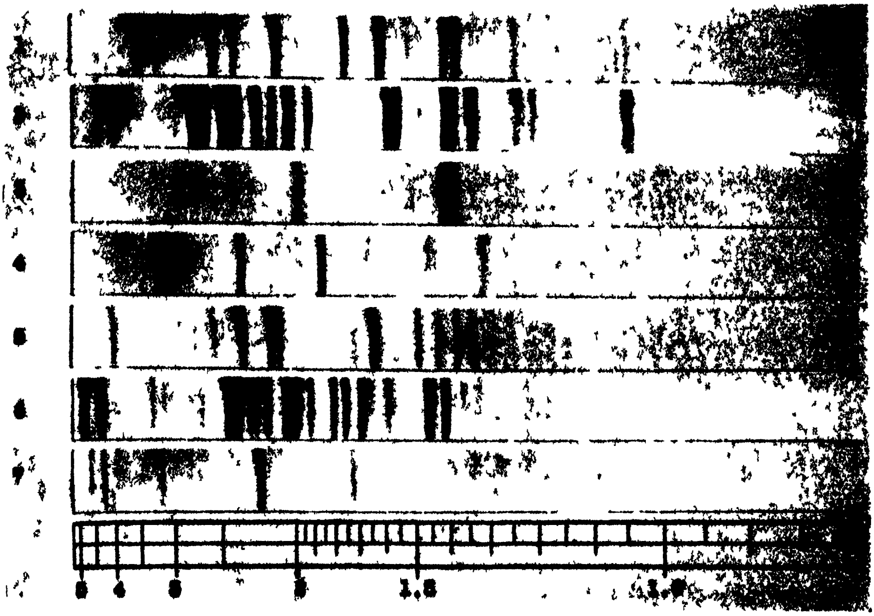

FIG. 1. X-RAY DIFFRACTION PATTERNS OF OXIDES AND HYDRATES OF ALUMINUM

1, α-Al_2O_3, 2, β-Al_2O_3, 3, γ-Al_2O_3, 4, α-$Al_2O_3 \cdot H_2O$, 5, β-$Al_2O_3 \cdot H_2O$, 6, α-$Al_2O_3 \cdot 3H_2O$, 7, β-$Al_2O_3 \cdot 3H_2O$.

Another crystalline trihydrate, designated as beta-trihydrate, can be produced by saturating sodium aluminate solutions with carbon dioxide under certain conditions, and by other precipitation methods. Beta-trihydrate shows a different x-ray pattern than the alpha-trihydrate and differs also from it in solubility. It appears to be a metastable phase, and goes over to the alpha form on continued shaking or long standing in contact with alkali.

Aluminum monohydrate, in the form known as alpha-monohydrate, is found in many bauxites, of which the French bauxites are typical. Alpha-monohydrate can be produced by heating alpha-trihydrate with alkali or water under pressure.

Another crystalline form of monohydrate is the mineral diaspore, and this form—carrying out the nomenclature previously employed—has been termed "beta-monohydrate." Beta-monohydrate has not yet been made synthetically, and we have not investigated it other than to make an x-ray pattern of a typical sample.

The x-ray patterns, according to the powder method, given by the various forms of alumina and the hydrates, are shown in figure 1.

THE MONOHYDRATES

Weiser and Milligan's conclusion that there is no monohydrate other than diaspore, is controverted by the fact that millions of tons of the alpha-monohydrate, described above, are found in nature (4), and by its synthetic production on a large scale. Its crystal pattern, as will be seen from the figure, corresponds to the so-called delta-alumina of Weiser and Milligan.

When the trihydrate is heated in water containing small amounts of sodium hydroxide, it is rapidly converted into alpha-monohydrate (5). For example, alpha-trihydrate, when heated for about twenty hours, more or less, in a solution of sodium hydroxide at a temperature of about 170°C., is converted substantially to monohydrate. The product, after washing and drying at 105°C., has a water content of about 16 per cent ($Al_2O_3 \cdot H_2O$ = 15 per cent H_2O). In this method the water content is reduced from the 34.6 per cent of the trihydrate to 16 per cent by heating in water. Apparently the product contains a small amount of adsorbed water. The monohydrate also may be approached from the other direction. The trihydrate was heated in air at 600°C. for one hour and the water content was reduced to 1.6 per cent; on x-ray examination this product showed the presence of some gamma-alumina but no other x-ray pattern. This dehydrated product was then digested in water plus sodium hydroxide at 150°C. for about fifteen hours, washed and dried at 105°C. This product had a water content of about 16 per cent and showed only the x-ray pattern we attribute to alpha-monohydrate. These experiments offer definite evidence of the existence of the alpha-monohydrate.

If a small amount of trihydrate is heated in air, most of it decomposes to an amorphous form, but if it is heated in sufficient bulk so that enough water vapor stays in contact with the material, some recrystallization to alpha-monohydrate may occur, but usually only a small percentage is so converted. The water content of the mixture can be reduced to 15 per cent or to 10 per cent, or to other values by changing the time and conditions of heating. Since an amorphous phase does not produce a diffraction pattern, the pattern of such a mixture is that of the monohydrate phase.

Very long aging in water at 100°C., as shown in Weiser and Milligan's experiment of aging for 1009 hours, will produce some alpha-monohydrate from amorphous alumina (their table 7 and figure 7). Weiser and Milligan's product, treated in this manner after drying at 50°C., had a water content of 19.35 per cent, and after heating for three hours in air at 160°C., it had a water content of 10.38 per cent. This product they considered to be either a new form of alumina with adsorbed water, or perhaps a hemihydrate. A mixture of about 70 per cent alpha-monohydrate with 30 per cent of amorphous alumina would have a water content of 19.50 per cent if the amorphous phase carried about 30 per cent adsorbed water. Upon drying such a mixture at 160°C., the adsorbed water would probably be substantially all removed without affecting the combined water of the very stable monohydrate, and the mixture would apparently have a combined water content of about 10.5 per cent. Here again, the amorphous phase does not produce a diffraction pattern, and the pattern of such a mixture is that of the monohydrate phase. Weiser and Milligan's conclusion that their "delta-alumina" is not a monohydrate seems to have come from the assumption that they had only one phase in their mixture dried at 160°C. (water content 10.38 per cent), since they got only one crystal pattern from such a mixture.

Confirmatory evidence for the existence of the alpha-monohydrate, as made by Tosterud's method, is presented by the thermal arrests observed on heating. If about 100 g. of the compound are placed in a crucible and heated in an electric furnace, an interesting series of observations is obtained from a sensitive thermocouple inserted in the mass. The time-temperature curve is smooth (see "C," figure 2) until a temperature of about 450°C. is reached, when an arrest showing heat absorption is recorded. This is the point where rapid decomposition of the monohydrate occurs. If trihydrate is heated, a similar decomposition point is observed at about 300°C. The decomposition point of the monohydrate is just as characteristic and reproducible as that for the trihydrate. Of course, the trihydrate and monohydrate will lose some water on heating at temperatures below these points, but the decomposition becomes quite rapid at the temperature range in question. The monohydrate is more stable at elevated temperatures than the trihydrate. The evidence for the existence of the alpha-monohydrate is just as complete, and parallels that for the alpha-trihydrate. Similar thermal arrests have been recorded by others in experiments of this character.

In figure 2 are also given heating curves for bauxites of two types. One, a trihydrate bauxite, gives a thermal arrest at about 250°C., and the other, a monohydrate bauxite, gives an arrest at about 425°C. The arrests observed with bauxites are usually somewhat lower than those observed with the pure hydrates. Other bauxites are known which contain both monohydrate and trihydrate, and the heating curves show both arrests. Furthermore, a heating curve made with trihydrate, if carried high enough and under proper conditions, sometimes shows a slight arrest at about 450°C., indicating the formation of some monohydrate from the trihydrate during the heating, but a curve made with pure monohydrate never shows the lower arrest.

The samples prepared by Weiser and Milligan according to Hüttig's procedure (K_1', K_1'', K_2, K_3, K_4 and L_3, figure 6) have an x-ray pattern which corresponds very closely to that of beta-trihydrate given in our figure 1. Additional discussion of beta-trihydrate is given in the article (2) previously referred to.

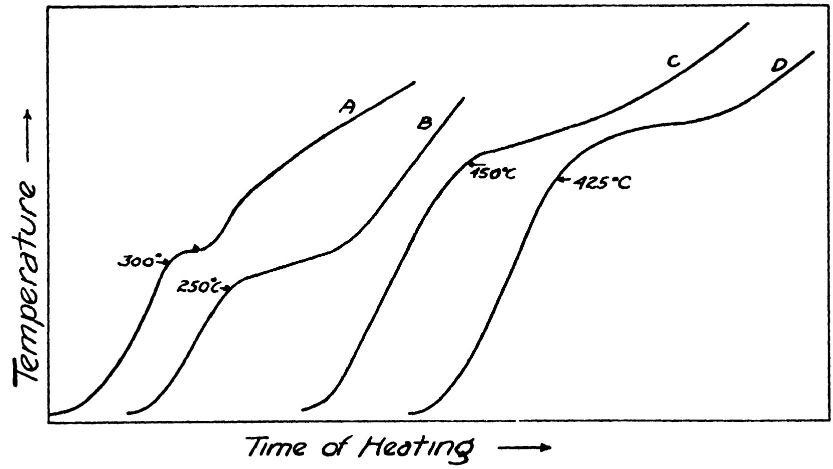

FIG. 2. HEATING CURVES

A, aluminum trihydrate; B, Arkansas bauxite; C, aluminum monohydrate; D, French bauxite.

While we have made no investigation of other forms of hydrate reported in the literature and reviewed by Weiser and Milligan, it seems quite likely, as they have concluded, that they are mixtures of other known hydrates, or incompletely crystallized products. Crystallization or recrystallization from a solid phase is attended with more difficulties than crystallization from a solution. In the conversion of precipitated amorphous alumina to a crystalline hydrate, there may be lines appearing in the x-ray diffraction pattern, or differences in the intensity of lines, which are caused by some incompletely crystallized product, and which can hardly be said to represent a new hydrate.

The x-ray data contributed in this paper are the work of W. L. Fink and K. R. Van Horn.

SUMMARY

There is a monohydrate of aluminum, $Al_2O_3 \cdot H_2O$, other than diaspore, and it is found widespread in nature and is being made commercially. Its existence can be demonstrated by chemical analysis, x-ray diffraction patterns, and thermal analysis.

Other forms of alumina and its hydrates are briefly reviewed.

REFERENCES

(1) Weiser, H. B., and Milligan, W. O.: J. Phys. Chem. **36**, 3010 (1932).

(2) Edwards, Frary, and Jeffries: The Aluminum Industry—Aluminum and its Production, p. 164. McGraw-Hill Book Company, New York (1929).

(3) Barlett: J. Am. Ceramic Soc. **15**, 361 (1932).

(4) Harder, E. C.: Ores of Aluminum, Chapter IV, p. 60, in The Aluminum Industry. McGraw-Hill Book Company, New York (1929)

(5) Tosterud, M.: Canadian patent 285,147; November 27, 1928

THE STANDARD BATTERY

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A steady current is quite essential for precise potentiometric measurements (1). We observed that storage batteries gave a fairly constant current for certain portions of the discharge but were quite sensitive to temperature variations. This suggested the idea of using the combination due to E. Weston (U. S. patent 294824), Cd Am / $CdSO_4$ (saturated at 4°C.) / Hg_2SO_4 / Hg, which has practically no temperature coefficient of E.M.F. for ordinary temperature ranges. We made two of these batteries with cathode areas of 100 $cm.^2$, which when closed in series over a potentiometer current of 20,000 ohms gave us a current which was exceedingly constant for hours at a time, requiring no adjustment of the regulating resistance, and permitted measurements of E.M.F. to microvolts.

After a few months use the above batteries showed a markedly decreasing E.M.F., but on adding some sulfuric acid to the neutral electrolyte the E.M.F. soon returned to normal and remained quite constant, indicating that an acid electrolyte is essential to prevent the hydrolysis of the mercurous sulfate and resulting disturbances.

At that time we gave most attention to the area of the cathodes and concluded that 100 $cm.^2$ cathode area would deliver satisfactorily one-tenth of a milliampere. Now we have obtained more experience and information about these batteries and find that attention should also be given to the polarization at the anodes of these batteries. Indeed the anode polarization appears to be the greater and we have sought for the most suitable ratio of anode and cathode areas for a desired current.

To this end we made standard batteries as follows. A 30-cm. (diameter) crystallizing dish was used and enough mercury added to cover the bottom of the dish. For the anode we used a 19-cm. "petri" dish that has a depth of only about 15 mm. and was partly filled with a 10 per cent cadmium amalgam. This anode was supported above the mercury cathode on a tripod made from glass rods. To further increase the anode area we stacked up several of these dishes, separating them by glass triangles made from 4-mm. glass rods. This battery was also provided with an independent small reference anode 1.5 cm. in diameter, so as to measure the polarization of anode or cathode independently when the battery was delivering a current.

Any current from these batteries will cause some polarization so that there is a drop in the E.M.F. if one is measuring to microvolts, but the drop occurs in less than one-half a minute and then the E.M.F. and current remain quite constant and satisfactory. When the current is interrupted these batteries soon regain their original E.M.F., even though they have been short-circuited and have delivered a much greater current than they were designed to give. Indeed, these batteries may serve as a quite satisfactory laboratory standard of E.M.F. which is independent of ordinary temperature changes, but they must be calibrated if one is concerned with the fourth decimal place in voltage.

To test the possibilities of these batteries we constructed two units as described below with cathode area of 666 cm.^{2} On a low glass tripod was placed a petri dish half-filled with 10 per cent cadmium amalgam with an anode area of 40.8 cm.^{2} A pilot anode served to determine separate polarizations. This battery showed a voltage of 1,018,100 microvolts and when closed over 20,000 ohms, promptly fell to 1,017,960 mmv. and was observed for 30 minutes with the results shown in table 1. All results are expressed in microvolts or 10^{-6} international volts.

TABLE 1

TIME	VOLTAGE	P_C	P_A
minutes	*mmv*		
0	1,018,100	0	0
1	1,017,946	−4	−150
2 0	1,017,951	−7	−142
3 0	1,017,952	−7	−141
5 0	1,017,945	−7	−148
10	1,017,950	−6	−144
15	1,017,945	−9	−146
20	1,017,946	−7	−147
25	1,017,946	−8	−146
30	1,017,945	−8	−147

Table 1 gives some interesting and unexpected results. The polarization at the 40.8 cm. anode area was some 147 mmv. for a current of 0.0001 amp., while at the 666 cm.^{2} cathode the polarization was only 7 mmv. We had expected quite different results, so we replaced the 40.8 cm.^{2} anode petri dish with one with an area of 293 cm.^{2}, but the anode still showed markedly greater polarization than the cathode. So we proceeded to stack up four of the anode dishes, giving a total anode area of 1300 cm.^{2} to 666 cm.^{2} cathode area. The anodes were connected together and acted as a unit, while the 1.5 cm.^{2} pilot anode served to measure the polarization of both anode and cathode. The results are given in table 2. The polarization of the anode with about twice the area of the cathode is still somewhat greater than the cathode, but this battery with an anode area some twice as great as the cathode area seems to be a satisfactory one. We proceeded to get more detailed information on it. Measurements such as those in tables 1 and 2 were made when the above battery was closed over various resistances and the results are summarized in table 3.

TABLE 2

Cathode area 666 cm.² Anode area 1300 cm.² 5000 Ω 0 0002 Ampere | Ω

TIME	P_A	P_C	P_{cell}	E M F CELL
		mmv	*mmv*	*mmv*
0	0	0	0	1,017,687
1	−109	−81	−189	1,017,498
3	−110	−82	−192	1,017,495
5	−108	−82	−190	1,017,497
10	−108	−91	−199	1,017,488
15	−104	−95	−199	1,017,488
20	−106	−91	−197	1,017,490
25	−107	−94	201	1,017,486
30	−101	−101	202	1,017,485
	−105	−92		1,017,489 ± 3

TABLE 3

Battery No. 2 Anode 1300 cm.² Cathode 666 cm.²

INITIAL E M F	RESISTANCE	CURRENT	AVERAGE E M F FOR HALF-HOUR	VARIATION OF E M F IN MMV OVER ONE HALF-HOUR
mmv	*ohms*	*milliamperes*	*mmv*	*mmv*
1,017,687	5000	0 2	1,017,490	±3 8
1,017,678	3000	0 33	1,017,371	±3 1
1,017,681	1000	1 0	1,016,806	±7 0
1,017,688	500	2 0	1,016,000	±5 0
1,017,667	250	4 0	1,014,371	±3 2
1,017,711	150	6 67	1,012,302	±1 5
1,017,698	100	10 0	1,009,786	±3 0
1,017,719	50	20 0	1,002,453	±10 0

The above results show a quite satisfactory performance. The polarization of course increases with the current drawn, but variation of the current, for the first half hour, decreases with increasing current; above 10 milliamperes it begins again to increase. With 150 ohms in circuit, or a current of 6.67 milliamperes, the variation of the current was only 1.5 parts in a million. This is a current of 1 milliampere for 100 cm.² of cathode area and 200 cm.² anode area, and represents the best performance. Even with a discharge of 20 milliamperes we had a constancy of one part in

100,000, a constancy that is quite unapproachable with any other battery or source of current.

Our experience and observations suggest the following specifications for these standard batteries. Owing to the size and structure of standard batteries they are not readily movable and so are best set up when they are to be used unless it is feasible to "wire" them to the point of use.

A satisfactory unit may be made in a 30-cm. diameter crystallizing dish, some 15 cm. deep, and with a flat bottom so that a minimum of mercury will continuously cover the bottom. Some 5 kilograms of mercury will be satisfactory. The best grade obtained from supply houses will suffice. The electrolyte should be acid by some 0.08 molar sulfuric acid and saturated with cadmium sulfate at approximately 4°C. Add 400 cc. of 1.84 density sulfuric acid to 4000 cc. of water and in this dissolve 5 kilograms of a good grade of $CdSO_4 \cdot 8/3\ H_2O$. The rate of solution of cadmium sulfate is remarkably slow, but overnight agitation with a motor-driven stirrer is effective. This gives some 5.4 liters of the electrolyte and covers the mercury in the 30-cm. dish to a depth of some 8 cm. From glass rods one may readily construct a low form of tripod that will support a 19-cm. petri dish a couple of centimeters above the mercury surface. The 19-cm. petri dishes are filled with enough 10 per cent cadmium amalgam to cover the bottom (some two kilograms of 10 per cent amalgam for 19-cm. petri dish). Four such dishes are stacked on the tripod, separated by triangles made from 5-mm. glass rods or tubes.

The amalgams are all connected to one binding post, while a wire protected by a glass tube connects the mercury cathode to the positive binding post. This mercury cathode is to be covered at all points with a thin layer of mercurous sulfate. The depolarizer requirements are not as exacting as for standard cells. The crystalline product (2) gives somewhat the best results, but the electrolytic product (3) is good, as is also the chemically prepared. One needs some 40 g. of mercurous sulfate for 100 cm^2 cathode area, so our unit in a 30-cm. dish requires some 300 g. of mercuric sulfate.

This may be made electrolytically (3), or satisfactorily as follows. To a liter of water in a suitable Erlenmeyer flask add 100 cc. of sulfuric acid (density 1.84), and in this dissolve 360 g. of mercuric sulfate ($HgSO_4$). From a tank of the liquid, bubble sulfur dioxide into this solution, reducing the mercuric sulfate, which at once begins to precipitate as a white product. When the mercuric sulfate is all reduced the sulfur dioxide begins to reduce mercurous mercury in fine globules. This finely divided mercury becomes entangled in the precipitate and gives it a gray color. When the product is a good slate gray the flow of sulfur dioxide is stopped, and the flask placed on a water bath with a motor driven stirrer. About 50 cc. of mercury was added to the system, which may be stirred at water bath temperature overnight. This permits the very fine globules of mercury, which have a greater solution tension than mercury (owing to surface tension) to go into solution and separate out on larger globules. Also there is a considerable recrystallization of the mercurous sulfate, owing to surface tension effects (4). This gives some 300 g. of mercurous sulfate, which is brought on to a Büchner filtering funnel, and the acid removed from it by suction. The cake of mercurous sulfate is just covered with a minimum of the electrolyte in which it is to be used, and this is drawn through with good suction, repeating two or three times. The cake is readily removed, freed from the filter paper and brought into the battery, where it disintegrates and tends to spread on the mercury cathode so that a satisfactory layer of the depolarizer is readily attained. When the anodes are put in place the battery is ready for use. The 30-cm. dish should have a good rim so that it may be tightly covered with a glass plate to prevent evaporation from the electrolyte. The electrolyte is nearly saturated with cadmium sulfate and a little evaporation would soon cause the crystallization of $CdSO_4 \cdot 8/3\ H_2O$, while the favorable temperature coefficient depends on the definite concentration of the $CdSO_4 \cdot 8/3\ H_2O$. With a little vaseline one may make sure that there will be no evaporation. On a high resistance circuit, i.e., over 20,000 ohms, two of these batteries have given excellent service for years. Some mercurous sulfate has been used up and the electrolyte has become slightly more concentrated. If one keeps a rough account of the current drawn, one may at any time by a simple calculation arrive at the amount of mercurous sulfate to add and the amount of water needed to dilute the electrolyte so as to restore the original condition. The E.M.F. of one of these batteries on open circuit, after it has rested for several hours, is a good criterion of the state of the electrolyte.

REFERENCES

(1) Hulett, G. A.: Phys Rev. **27**, 34 (1908).
(2) Elliott, R. B., and Hulett, G. A.· J. Phys Chem. **36**, 2083 (1932).
(3) Hulett, G. A.: Phys. Rev. **32**, 262 (1911)
(4) Hulett, G. A.: Z. physik. Chem. **37**, 385 (1901).

A SIMPLE METHOD FOR ACCURATE DETERMINATIONS OF VAPOR PRESSURES OF SOLUTIONS

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INTRODUCTION

The importance of vapor pressure in the study of solutions warrants a far more extensive exploitation of this property than has yet been made. Many attempts have been made to evolve practical and accurate means of determination, but the amount of reliable data so far accumulated is very scanty indeed. Hitherto facility and accuracy appear to have been incompatible.

Undoubtedly the most accurate determinations of vapor pressure lowering, to date, are those of Lovelace, Fraser and coworkers (1), who by rigorous care in the removal of air and using a reliable sensitive manometer seem to have attained an accuracy to the order of less than 0.001 mm. The method is too elaborate for general application, but for standard determinations it has, as yet, no equal.

Reviews of the older methods are available in the literature. Recent determinations may be mentioned briefly.

Bousfield and Bousfield (2) used an apparatus which was very neat and compact, but these authors appear not to have appreciated fully the errors arising from residual air, and errors to the extent of nearly 10 per cent of the lowering are evident in the region of lower concentration. The pressure of residual air may be much greater than that indicated by the volume of the bubble of air remaining when the solutions have been brought to atmospheric pressure.

The most advanced development of the dynamical method has been made by Pearce and Snow (3). The accuracy attainable is of the order of 0.01 mm., but by taking a mean of several observations, values reliable to within a few thousandths of a millimeter may be obtained.

The dew-point method used recently by Hepburn (4) seems to be capable of useful application. An accuracy of 0.03 mm. is estimated. A method described by Hill (5), depending on the principle of the wet and dry bulb thermometer, may prove useful for some purposes. With moderately concentrated solutions the estimated accuracy is 2 per cent.

The limited accuracy of the various methods may be gauged from the fact that at 25°C. the molecular lowering for solutions of such salts as potassium chloride is only about 0.75 mm.

BOUSFIELD'S ISOPIESTIC METHOD

In the paper referred to above, Bousfield makes mention of a method for comparing the vapor pressures of solutions, called the "isopiestic" method and described in earlier papers. This method is apparently so simple that the absence of further mention of its application would appear to indicate that it did not fulfil expectations. According to Bousfield, four open cylindrical glass vessels containing different solutions are placed in a desiccator vessel, which is evacuated and placed in a thermostat for two or three days. By this time the solutions will have come into equilibrium by distillation of water, so that each will have the same vapor pressure. The concentrations are determined by weight and hence, if accurate data are available for one solution, equally accurate values may be assigned to the others. Results, apparently confirmatory, are quoted.

In order to test Bousfield's method, the author placed two crystallizing dishes containing respectively approximately 1 *M* potassium chloride solution and water in a vessel which was evacuated to 15 mm. and left for several days. The amount of distillation occurring was barely noticeable even when the dishes were floated on mercury, to aid temperature equalization. Presumably, the rate of distillation between two solutions differing in concentration by only 1 per cent would be 100 times as slow!

As pointed out by Bousfield, the attainment of equilibrium is dependent on the equalization of temperatures. When the air is removed the vapor pressures of all surfaces in the vessel must be the same, but the temperatures are different. However, the order of the magnitudes involved was apparently not realized. From data in the International Critical Tables the following calculations were made.

At 25°C. $\frac{dp}{dt}$ for water is 1.4 mm. per degree. Hence a pressure difference of 0.001 mm. at the same temperature corresponds to a temperature difference of 0.0007°C. at the same pressure.

The latent heat of vaporization of water at 25°C. is 2436 joules per gram. Therefore, if we have two surfaces differing in temperature by 0.0007°C. and separated by a medium of thermal conductance equivalent to one centimeter cube of the undermentioned materials, the times required for 1 gram of water to distil, or 2436 joules to flow, from one to the other may be calculated from the thermal conductivities (without convection) to be for (a) glass—10 years, (b) water—17 years, (c) gases—500 years, (d) mercury—15 months, (e) copper—10 days.

Considering these astonishing figures, it is surprising that the results quoted by Bousfield are as good as they are. Earlier papers show, however, that these figures were taken from series of experiments extending over several months, in which solutions were built up by distillation of water from the trough of the desiccator, weighings being made every two or three days. Apparently, no experiment was made to see if two solutions of the same salt came to the same concentration after two or three days and assumptions were made which were not sustained by later trials.

APPLICATION OF THE ISOPIESTIC METHOD

From the above considerations it would appear that the method as described by Bousfield is too slow to be suitable for practical application. However, by incorporating the following principles in the design of apparatus, it seemed probable that the method could be rendered practicable.

By providing good metallic conduction between the solutions, the retardation due to thermal resistance between them may be reduced to quite a small value. The factors limiting the rate of attainment of equilibrium would then be diffusion of solute and conduction of heat through the solutions. These could be accelerated by stirring and by making the solutions shallow. Too violent agitation is to be avoided, however, since minute heating effects would cause appreciable errors. Quantities of solutions as small as compatible with accuracy in weighing are also desirable, to minimize the amounts which have to distil.

THE METHOD ADOPTED BY THE AUTHOR

Preliminary experiments

Solutions of potassium chloride placed in silver-plated copper dishes fitting neatly together and mounted on a copper base were found to approach identity of concentration at quite a feasible rate, when rocked in an evacuated desiccator vessel in a thermostat. It was discovered that the rate was greatly increased by placing some solution in the crevices between the dishes. Evidently the temperature gradient here was reduced appreciably by the substitution of solution for vapor in the gaps. Using about 2-cc. quantities of approximately 1 *M* potassium chloride, it was found that a 25 per cent difference could be reduced to 1 per cent in twenty-four hours. During a series of experiments in which potassium chloride and cane sugar solutions were compared the following procedure was evolved.

Apparatus

The dishes were 1⅓ inches square by ¾ inch deep, a set of four being placed in square formation on a silver-plated block 1 inch thick. The block acted as a steadying heat reservoir as well as a conducting medium. The thermostat was believed to keep constant to about 0.01°C. at 25°C.

The variations need not necessarily be reduced to a very small amount, as the temperature waves are damped down considerably by the thick walls of the desiccator, and the massive copper block ensures that any small disturbance is equitably distributed. The heating lamp was blackened since the radiation, which had an appreciable effect on the regulator, would also be liable to affect the dishes and possibly maintain a permanent temperature gradient therein. The period and angle of oscillation were about 1 second and 20° respectively.

Procedure

The solutions were weighed into the dishes by pipetting in 2 cc. and weighing quickly to the nearest milligram. In the case of concentrated solutions the amount of solid in 2 cc. was sufficient to be weighed in directly with accuracy. In all determinations made, potassium chloride solutions were used as standard. Duplicates of each solution were inserted, being placed in diagonal opposition in the set, so as not to be in direct contact, and therefore to provide a more reliable mean.

Caustic soda of about the same concentration as the potassium chloride in the dishes was used as intermediate conducting solution, being preferred since it spread more easily over greasy surfaces.

The evacuation was effected by means of a water pump, the pressures being reduced to 15–20 mm. Complete removal of air is not required—merely sufficient to remove the diffusion retardation.

The dishes, on being removed from the desiccator, were kept covered while they were cooled rapidly in a stream of cold water and dried on the outsides with filter paper. An approximate weight was estimated, while still covered, and final weighing completed in a few seconds after removing the cover. Errors due to evaporation may amount to several milligrams and this is the largest error with the more concentrated solutions. A better plan would be to provide the dishes with permanent lids, but this refinement was not introduced at this stage.

The same set of solutions may be used to make as many as five or six determinations over a range of concentrations varying by about 40 per cent. The most convenient method of varying the concentrations, and that which gave the best results, was by distillation of water from the bottom of the desiccator. This distillation is chiefly indirect. The thermal conduction between the block and the walls of the vessel being poor, the block is heated from room temperature to 25°C. by distillation of water onto the block, from the water in the bottom which is heated more quickly. This water then distils into the dishes. Finally the block attains a slightly higher temperature than the thermostat and further distillation takes place into the solutions, at a rate depending on the flow of heat from the block to the thermostat. This is negligibly slow with dilute solutions, but is appreciable with concentrated solutions.

The removal of water by pumping off was difficult to accomplish satisfactorily. The best method was found to be to use high concentrations of intermediate solution.

The times required for the solutions to come sufficiently close to equilibrium vary according to viscosities, but other things being equal, rates of distillation should be proportional to the temperature difference. For the same percentage difference in concentration this is proportional to the concentration. For any one concentration the difference should be reduced equal fractions in equal times. With 0.5 *M* potassium chloride solutions the rate is greater than one-tenth in one day and so, if the solutions do not differ originally by more than 2 or 3 per cent, one day should be sufficient for an accuracy of 0.3 per cent. In general, one day was allowed for all solutions above 0.5 *M* and below this the times were increased, until at 0.1 *M* three days were allowed. This time gave uniform results.

Calculation of results

The actual calculations are simple, the molality being inversely proportional to the weight of water in the dish.

Potassium chloride was always taken as standard, the values obtained by Lovelace, Frâser and Sease (6) being taken as correct and assuming that the relative lowering is the same at 25°C. as at 20°C. The International Critical Tables state that the variation with temperature is inappreciable for this salt. The vapor pressure of water at 20°C. was taken as 17.535 mm.

Results are expressed in terms of molecular relative lowering, in conformity with the practice in the tables. The clearest method of exhibiting the results is by means of a graph, plotting molecular relative lowering against molality. Tables of values taken from the author's curves are provided to enable the curves to be reconstructed.

RESULTS

Cane sugar solutions

The choice of cane sugar as a solute for preliminary experiments was perhaps not the best, on account of the high viscosity of the solutions. Nevertheless, the results obtained were gratifyingly good.

The materials used were A.R. potassium chloride and a specimen of sugar prepared some years ago for research work in this College.

Determinations were made over a range of concentration from 0.2 *M* to 1.5 *M*, corresponding to 0.1 to 0.9 *M* potassium chloride. The results are shown in figure 1 and table 1. A better uniformity is desirable in the higher concentration region, but below 0.8 *M* the deviations from the smooth curve are less than 0.3 per cent, or less than 0.0007 mm. expressed as pressure. With three obvious exceptions the deviations in the higher region are of the order of 0.2 per cent., which at 1.4 *M* corresponds to about 0.0014 mm. Errors of 0.2 per cent are quite possibly introduced by losses by evaporation before weighing, and a better uniformity was not to be expected.

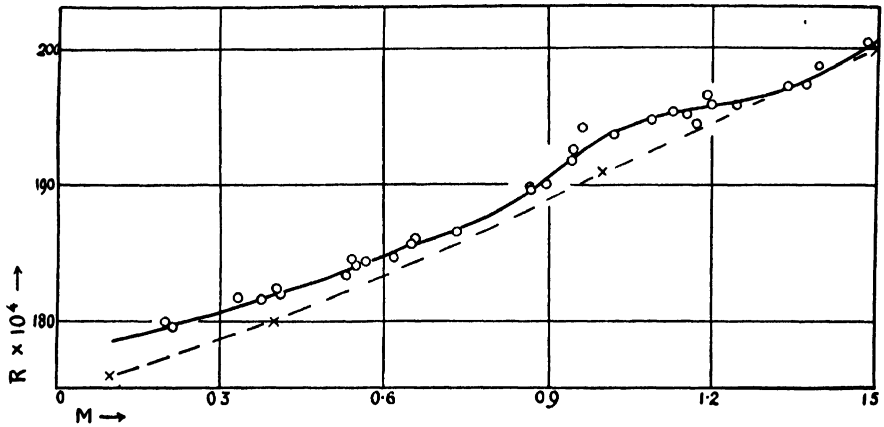

FIG. 1

TABLE 1

Values of $R = \frac{p_0 - p}{Mp_0}$ *for sucrose solutions, at 25°C.*

M (moles per 1000 grams of water)	$R \times 10^5$
0 2	1796
0 4	1821
0 6	1848
0 8	1881
0 9	1906
1 0	1936
1 1	1951
1 2	1959
1 3	1967
1 4	1985

The curve obtained from the few points given in the International Critical Tables is also shown in figure 1. The original paper was not available to the author, but the determinations were probably made with the Lovelace and Fraser apparatus. The difference is not great and, except for the elevation between 0.8 and 1.3 *M*, is less than 0.002 mm. Although the difference in the molal lowering becomes greater in the dilute region, the actual difference in pressure becomes smaller and at 0.2 M is only about 0.001 mm.

The elevation between 0.8 M and 1.3 M corresponds to the elevation in the standard curve for potassium chloride (see figure 3). It may be eliminated by allowing deviations of 0.002 mm. in the measurements of Lovelace, Fraser and Sease, but this would be altogether too revolting to these authors. The real existence of this irregularity is supported by the independent measurements on lithium chloride solutions made by Lovelace, Bahlke and Fraser (1), which show a similar irregularity. It has also been observed recently by Burrage (7) that there is a parallelism in the curve for the solubility of lead chloride in potassium chloride solutions.

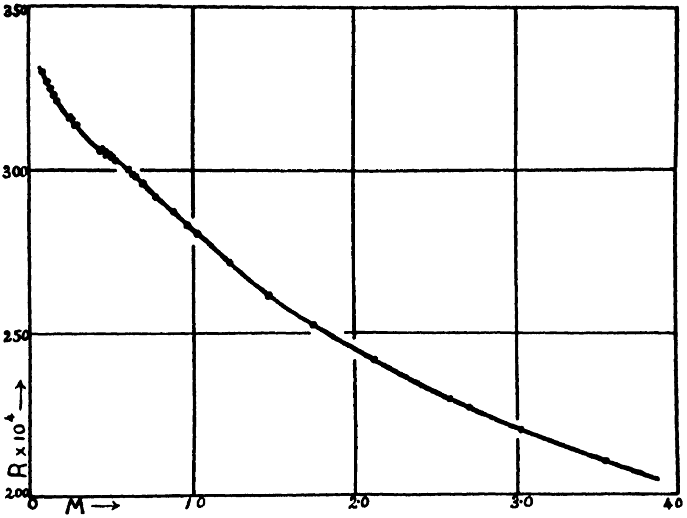

FIG. 2

The significance is uncertain, but it would appear that the irregularity is due to a property of water in this activity range which is independent of the type of solute. Further direct measurement in this region is highly desirable.

Sodium chloride solutions

A few determinations on sodium chloride solutions serve to show that the irregularity appears also in the curve for this salt. The author's determinations tend to confirm the values given in the International Critical Tables (original paper unavailable). Bousfield and Bousfield obtained values about 8 to 9 per cent higher.

The author's results are inserted as dots in figure 3.

Potassium toluene-p-sulfonate solutions

An extensive series of determinations was executed with solutions of this salt over a range of concentration from 0.1 *M* to saturation. The specimen used was some of a preparation used in previous research work in this College, and was taken as sufficiently pure without further test, other than that for water content. The salt crystallizes with one molecule of water of crystallization. This is, however, easily driven off. A sample of a batch dried at 130°C. in an air-oven for two hours did not lose weight further on being subjected to two hours' treatment with a stream of air under 20 mm. pressure at 130°C., dried over phosphorus pentoxide.

The results are exhibited in figure 2 and table 2. Satisfactory general uniformity was obtained. The distribution of points in the region of the irregularity unfortunately does not allow the exact shape of the curve to be determined here. The small irregularity, although quite evident, seems to be masked by a longer irregularity extending to 1.3 *M*, which may or may not be due to experimental error, since the five points from 0.79 *M* to 1.3 *M* were all obtained from one set only. Circumstances did not allow confirmation to be made.

TABLE 2

Values of R for potassium toluenesulfonate solutions, at 25°C.

M	$R \times 10^6$	*M*	$R \times 10^6$
0.1	3274	1.0	2820
0.2	3192	1.2	2727
0.3	3128	1.4	2641
0.4	3072	1.6	2572
0.5	3040	1.8	2508
0.6	3005	2.0	2450
0.7	2960	2.5	2316
0.8	2907	3.0	2210
0.9	2864	3.5	2118

The solubility of the salt does not appear to have been determined previously. From the vapor pressure of the saturated solution it was estimated by the author, by a short extrapolation, that the molality of the saturated solution was about 3.87.

COMPARISON OF MOLECULAR LOWERING CURVES

Figure 3 gives a comparison of the curves for five salts. The values for potassium nitrate and sodium chloride were taken from the International Critical Tables, while those for potassium and lithium chlorides are from the original papers previously referred to.

The comparison shows what wide variations exist among these simple salts with common anions and cations. A close parallelism between potassium nitrate and potassium toluenesulfonate is evident. Whether this is fortuitous or due directly to common properties of the sulfonic and nitrate ions must be decided by further investigations.

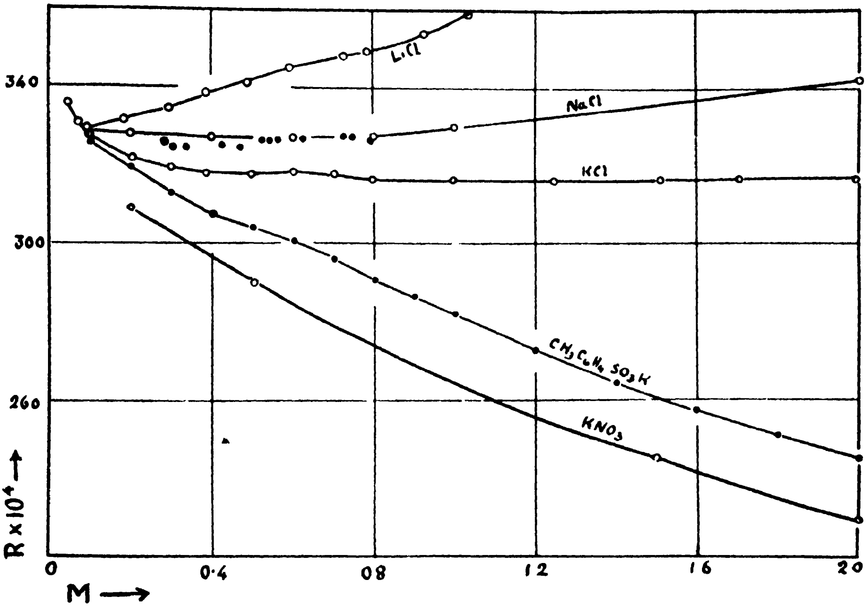

FIG. 3

CONCLUSION

The method described for determining vapor pressures of solutions appears to be capable of yielding results of a high degree of accuracy. The sensitivity is demonstrated by the clear discernment of irregularities, which are detected only by the most accurate direct measurements which have been made and are very close to the experimental error thereof. With greater refinement and care, even more accurate results should be obtainable, but for the present sufficiently good results are obtainable by the simple procedure described above.

The method should prove very useful in extending vapor pressure data, which are highly desirable and will become more and more important as the theory of solutions progresses into the more concentrated regions.

SUMMARY

Solutions may be brought rapidly into equilibrium as regards vapor pressure, and by taking one as a standard, values for the vapor pressure lowering may be obtained with an accuracy of 0.3 per cent or less for solutions of concentration above 0.1 *M*. Determinations have been made on solutions of sucrose, sodium chloride, and potassium toluene-*p*-sulfonate, using potassium chloride as standard.

The author desires to thank Professor F P Worley, under whose supervision this work was carried out, for his sustained interest, and for his assistance in preparing the paper for publication

REFERENCES

(1) Lovelace, Bahlke, and Fraser J Am Chem Soc **45**, 2930 (1923), and earlier papers
(2) Bousfield and Bousfield Proc Roy Soc London **A103**, 429 (1923)
(3) Pearce and Snow J Phys Chem **31**, 231 (1927)
(4) Hepburn J Chem Soc **1932**, 550
(5) Hill Proc Roy Soc London **A127**, 9 (1930)
(6) Lovelace, Fraser, and Sease J Am Chem Soc **43**, 102 (1921)
(7) Burrage Trans Faraday Soc **28**, 529 (1932)

THE INFLUENCE OF COMBINED OXYGEN ON THE ADSORPTION OF VAPORS BY POROUS SOLIDS. I

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I. INTRODUCTION

As a result of the development of the improved retentivity technique for the determination of isothermals (1), it has been found that the isothermals derived by this method consist of a series of sharply defined steps. The present investigation was undertaken to determine whether these rectangular steps could be obtained by the static technique. It has been stated previously (2) that carbon dioxide on the surface of the charcoal exerts a very disturbing influence on the breaks, and it seemed probable that the fact that the static isothermals heretofore had been found to consist of a series of curves might be due to this cause.

The difficulty of securing an oxygen-free surface has already been emphasized by the author (3), and in the present investigation the most elaborate care has been taken to obtain a charcoal surface as free from oxygen as possible. It has been found (4) that it is most difficult to remove the C_xO_y from an underactivated charcoal, and it was therefore decided to carry out the present investigation with a charcoal of this type, as, provided that the oxygen could be removed in this case leaving a charcoal yielding an isothermal of rectangular steps, then the same result might be expected with other charcoals. Charcoal D1 (5) was therefore chosen, since it fulfilled the necessary conditions.

EXPERIMENTAL

Since the experiment would probably involve the detection and measurement of small quantities of carbon dioxide, it was decided to effect this by means of the Pirani gauge technique. It was, therefore, necessary first of all to obtain the coefficient for carbon dioxide so that the $f(v)$ readings might be converted to pressures. In the cases of carbon tetrachloride (see Chaplin (6)) and carbon disulfide (determined by the author) the value of α has been found to be constant up to 0.2 mm. The Pirani measurements were carried out in the manner described by Chaplin (6) and the carbon dioxide pressures read off on a McLeod gauge of the type described by the same author (7). The results are given in table 1 and it is seen that the coefficient for carbon dioxide is constant up to a pressure of 0.06 mm., but at higher pressures the value steadily increases.

The experimental train employed in the main investigation was as follows:

A. Hyvac oil pump
B Leybold diffusion pump
C. McLeod gauge.
Two-way tap

D. McLeod gauge.
E Purifying charcoal and manometer tube.
F. Carbon tetrachloride supply bulb.
G. Freezing tube.
H. Pirani gauge.
I. Container in oven

K Freezing tube.
L Pirani gauge
M. Measuring apparatus in thermostat at 25°C.

TABLE 1

$f(v)$	p mm	α
9 70	0 377	0 039
6 218	0 218	0 035
4 707	0 160	0 034
3 057	0 094	0 031
2 309	0 065	0 028
1 427	0 038	0 027
0 724	0 021	0 028
0 705	0 019	0 027
0 357	0 0092	0 026
0 181	0 0048	0 027
0 065	0 0018	0 027

The technique employed in the filling and weighing of the charcoal container is the same as in the previous experiment (2). A to I comprise the complete apparatus used in removing oxygen and charging with carbon tetrachloride. The general technique employed was as follows. The charcoal was evacuated at room temperature to zero pressure and then for eighty hours at 800°C., till a pressure of 10^{-4} mm. was attained. Carbon tetrachloride was then liberated from the supply bulb F, which contained charcoal saturated with carbon tetrachloride and closed by a tap from the main apparatus. This vapor was separated from carbon dioxide by freezing out the carbon tetrachloride with melting methylcyclohexane at G. This carbon dioxide was adsorbed by the purifying charcoal E in the manner described by Chaplin (6). The evacuated charcoal was charged to saturation at 50 mm. pressure and the temperature of the oven raised to 50°C., the container tap being shut.

After standing at this temperature for some hours, the container tap was opened with liquid air on the freezer G. When equilibrium had been established the container tap was shut and the carbon monoxide pressure read. This was pumped away and the liquid air on the freezer replaced by melting methylcyclohexane. The pressure of the carbon dioxide was thus obtained. $CO = 4.5$ mm., and $CO_2 = 0.06$ mm.

The carbon dioxide was removed and the carbon tetrachloride allowed to stream back on the charcoal at room temperature. The container tap was again shut and the temperature raised to 100°C. and kept at this figure for five hours. The tap was then opened and the carbon monoxide and carbon dioxide measured as before. $CO = 5.0$ mm., $CO_2 = 3.5$ mm. These gases were pumped away and the carbon tetrachloride allowed to stream back on to the cooled charcoal. This process was repeated and the analysis gave 1 mm. CO and 0.03 mm. CO_2. This was pumped away as before, and the process again repeated, the analysis being $CO = 5 \times 10^{-3}$ mm. and $CO_2 = 1 \times 10^{-2}$ mm. Since this is the total removed, the actual pressure over the charcoal must be negligible. In order to see if all the oxygen had been removed from the charcoal, the container was heated for nine hours at 140°C., 1 mm. of CO and 2 mm. of CO_2 being obtained. Obviously after all this drastic treatment the charcoal is not oxygen-free. The isothermal should, however, be practically unaffected by the amount of oxygen which remains. The quantity of carbon tetrachloride adsorbed was 266.9 mg. per gram.

It has been pointed out before that carbon dioxide exerts a poisoning effect and therefore all charcoal isothermals which have been obtained heretofore are affected to a greater or lesser extent, the quantity figures being too small in all cases. The above results are at variance with the claims of previous workers that an oxygen-bare surface can be obtained by evacuation at 900°C. for twenty-four hours, since in the present instance, by flushing out with vapor, a total pressure of 14 mm. of combined oxygen has been generated after a preliminary evacuation of 800°C. for eighty hours.

The other arm of the two-way tap connects with a freezer K, a Pirani gauge L and an apparatus M, similar to that described in a previous publication (figure 1 in reference 2) from A to G, with the exception of the freezer C. A distinct improvement has been made in the apparatus, in that the whole is immersed in a glass-sided thermostat at 25°C. The calibration of the volume was carried out at this temperature and as a wide manometer was employed, a volume correction was applied for each reading. The volume of the bulb N was 53.3 cc. and the volume of the main apparatus 66.5 cc. at zero pressure. The quantities were calculated

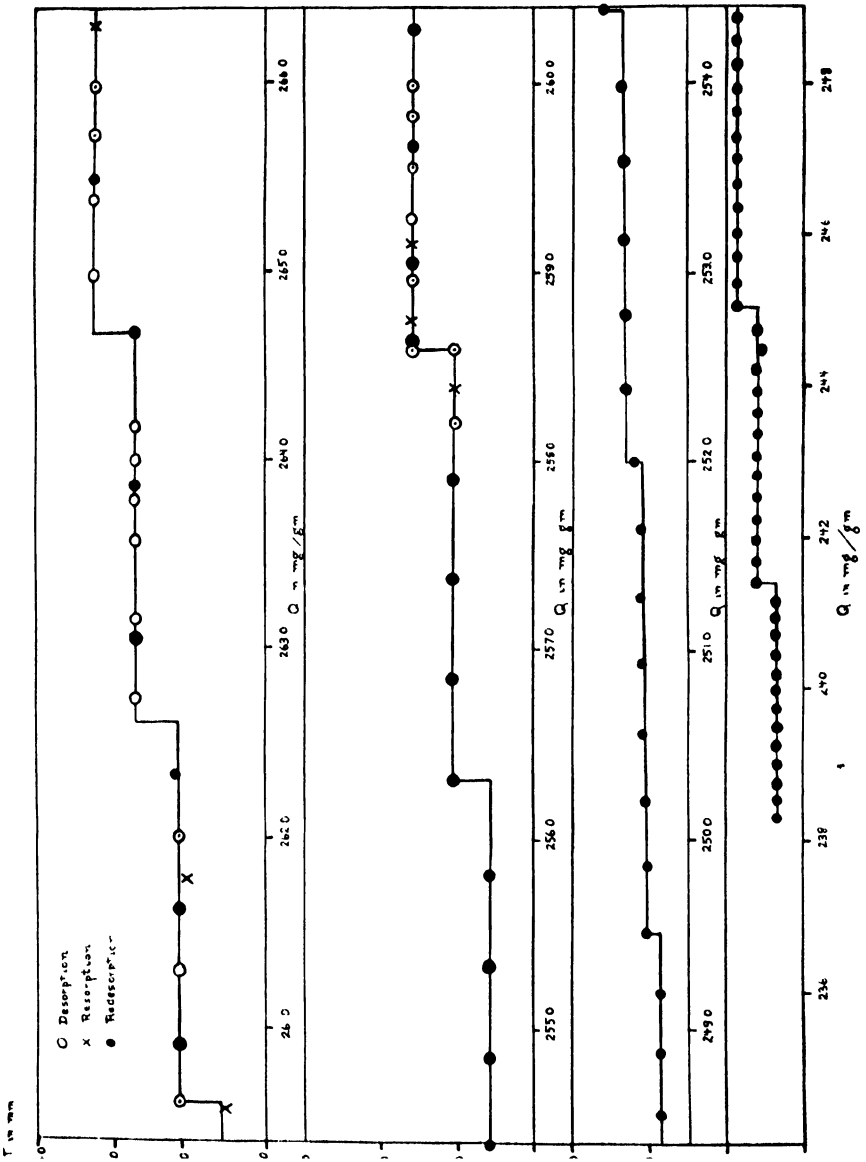
T in mm
O Desorption
x Resorption
● Redesorption
2610
2620
2630
2640
2650
2660
Q in mg/gm
2550
2560
2570
2580
2590
2600
Q in mg gm
2490
2500
2510
2520
2530
2540
Q in mg gm
236
238
240
242
244
246
248
Q in mg/gm

FIG. 1

by the pressure change method (2), and the pressures are considered to be correct to 0.01 mm. It has been found that over certain ranges of sorption values the dead space volume can be increased during desorption, or diminished during resorption, without alteration of pressure.

The complete results comprise a desorption curve, followed by resorption and further desorption, the resultant isothermal being shown in figure 1.

The figures obtained at the higher pressures are given in table 2 in the order in which they were obtained and show the degree of reversibility which has been attained.

TABLE 2

P	Q	P	Q
mm	*mg per gram*	*mm*	*mg per gram*
5.24	265.98	3.01	258.19
5.23	265.72	3.03	258.38
5.24	265.37	3.59	258.74
5.23	264.98	3.59	259.15
4.70	264.17	3.54	260.57
4.71	264.00	4.00	261.78
4.70	263.79	4.70	263.83
4.70	263.58	5.22	266.30
4.70	263.15	5.22	265.48
4.70	262.73	4.71	264.67
4.12	262.01	4.71	263.86
4.12	261.30	4.71	263.05
4.12	260.60	4.18	262.33
3.56	259.99	4.12	261.62
3.57	259.82	4.12	260.91
3.58	259.55	3.56	260.29
3.58	259.28	3.56	259.67
3.57	258.96	3.56	259.05
3.38	258.59	3.56	258.63
3.02	258.59	3.07	257.90

At the close of the experiment a check weighing was carried out and a comparison made with the quantity calculated by the pressure change method.

	mg per gram
By weight	238.5
By pressure change	238.28

In view of all the stages involved this is good agreement.

DISCUSSION

As will be seen from figure 1, a most important fact has resulted from this experiment, in that isothermals on charcoal obtained by the static technique consist of a series of rectangular steps. It has already been shown that this type of isothermal is obtained by the improved retentivity technique, instead of a series of curves as had been previously obtained by both static and retentivity techniques.

It is clear, therefore, that this true structure of the charcoal isothermal only results when the surface is free or almost free from foreign adsorbed matter. During the whole of the course of this experiment no trace of carbon dioxide was detected when the carbon tetrachloride had been frozen out. Another very interesting point was the rate of attainment of equilibrium, which was instantaneous during both sorption and desorption, no change being detected after standing for seventy-two hours. The isothermal was found to be absolutely reversible, which is again of interest, since previously (8) marked drift had been found with carbon tetrachloride isothermals on this charcoal.

A discussion of the pressure intervals of the breaks and the quantity values of the steps will be deferred until a later publication. For obvious reasons it is extremely difficult to get two points on the vertical section, but this has been achieved at a $Q = 258.59$ mg. per gram, thus justifying the drawing of vertical portions in other instances. In each case, however, the exact value lies between two adjacent points, the quantity taken being arbitrarily chosen.

It has been mentioned in a previous publication (5) that the reason why breaks had not been found by other workers was due to insufficient points being determined on the isothermal. The author improved on this by taking 350 points in a range of 81 mm. (2), and in the present paper 100 points have been obtained in a pressure range of approximately 4 mm. This fact, together with the reversibility which has been obtained, leave no doubt as to the true structure of the isothermal on charcoal.

SUMMARY

1. The coefficient for carbon dioxide has been determined by the Pirani gauge technique.

2. The charcoal was very thoroughly evacuated and freed from oxygen as completely as possible by flushing with vapor.

3. A carbon tetrachloride isothermal was obtained by the static technique at 25°C., comprising rectangular steps.

4. Reasons have been advanced for previous isothermals being found to consist of a series of curves.

REFERENCES

(1) Burrage: J. Phys Chem **37**, 33 (1933).
(2) Burrage: J. Phys. Chem. **36**, 2272 (1932).
(3) Burrage: Trans Faraday Soc. **28**, 192 (1932).
(4) Burrage: Unpublished.
(5) Burrage: Proc. Roy. Soc. London **130**, 610 (1931).
(6) Chaplin: Proc. Roy. Soc. London **A121**, 344 (1928)
(7) Chaplin: Phil. Mag. **2**, 1198 (1926).
(8) Allmand and Chaplin: Proc. Roy. Soc. London **129**, 235 (1930).

THE TRANSITION POINTS OF SALT HYDRATES IN VARIOUS NON-AQUEOUS SOLVENTS

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Many methods have been used to determine the transition points of polymorphous solids and of salt hydrates. For both types of systems conductance methods have been used in various forms, taking advantage, particularly, of the difference in conductance due to the different solubilities of the two forms. In an earlier paper (1) it has been shown that with a constant amount of solvent and solute a break occurs in the resistance-temperature curve at the transition point when the solution of a salt hydrate in a non-aqueous solvent is heated over a short range of temperature in this region. The break in the curve is presumably due to the change both in the salt at this point and the simultaneous change in the solvent medium. The earlier study was limited to solutions of various concentrations in ethyl alcohol and alcohol containing small amounts of water. In the present paper are given results obtained with a number of additional salts in methyl, ethyl, propyl, and isoamyl alcohols, pyridine, acetone, and ethylene glycol.

APPARATUS, MATERIALS, AND METHODS

The cell used was in the form of a U-tube with the electrodes sealed in one arm and the thermometer placed in the other. The design permitted the solution to be transferred from one arm to the other to insure uniformity and obviated any change in the cell constant due to slight differences in proximity of the thermometer to the electrodes. The similar placement of the bulb of the thermometer and the electrodes, together with the very slow rate at which the temperature of the bath was increased, made it possible to assume that the temperature in both parts of the cell was the same. The thermometer was graduated in tenths of a degree and had been checked against a standard thermometer. Connection was made through the stopper bearing the thermometer with a mercury trap which prevented any loss of the vaporized solvent from the system and minimized concentration changes due to the high vapor pressure of the solvents.

The ethyl alcohol was prepared by allowing ordinary commercial alcohol to stand over freshly broken lime for several days, after which it was distilled over a slow water bath, only the middle portion being retained. The acetone was purified with sodium bisulfite and dehydrated in the usual manner. The other solvents and the salts used were all high grade products and no attempt was made to purify them further.

In most of the determinations saturated solutions were used. A quantity of the solvent was shaken for some time in a dried, air-tight container with an excess of solute and after being allowed to settle the clear supernatant liquid was transferred to the cell. In some determinations the saturated solution was diluted with pure solvent before being introduced into the cell, and in others less solute than that required to make a saturated solution was used. In each case the bath was brought up to a temperature a few degrees below the transition point of the salt before introducing the cell, after which the temperature of the bath was raised at the rate of about eight degrees an hour. Frequent readings of the resistance were then taken simultaneously with those of the temperature within the cell.

TABLE 1

$LiNO_3\ 3H_2O = LiNO_3\ \frac{1}{2}H_2O + 2\frac{1}{2}H_2O$ *in pyridine* (*series 1*), *in acetone* (*series 2*), *in amyl alcohol* (*series 3*)

$CaCl_2 \cdot 6H_2O = CaCl_2 \cdot 4H_2O\beta + 2H_2O$ *in propyl alcohol* (*series 4*)

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
22	1193	24	46 96	24 2	505 0	25	319 5
24	1181	25	46 77	25 3	492 9	26	314 3
26	1169	26	46 21	26	486 9	27	309 9
28	1157	27	45 84	27	473 4	28	305 5
30	1146	28	45 47	28	463 9	29	301 8
32	1137	29	45 11	29	454 7	30 1	296 9
34	1125	30	44 93	30	448 4	31 1	293 4
36	1116	31	44 57	31	438 6	32 1	288 7
38	1107	32	44 21	32	428 2	33 0	285 2
40	1099	33 2	43 68	33	419 7	34	281 8
		34	43 51	34	411 4	35	277 8
		35	43 16	35	403 2		

RESULTS

In table 1 are given the results obtained with lithium nitrate in pyridine, acetone, and amyl alcohol. In the first column of each series are given the temperatures and in the second the corresponding resistances. Plots were made of the various determinations, using both the resistances and the logarithm of the resistances as ordinates against the temperatures as

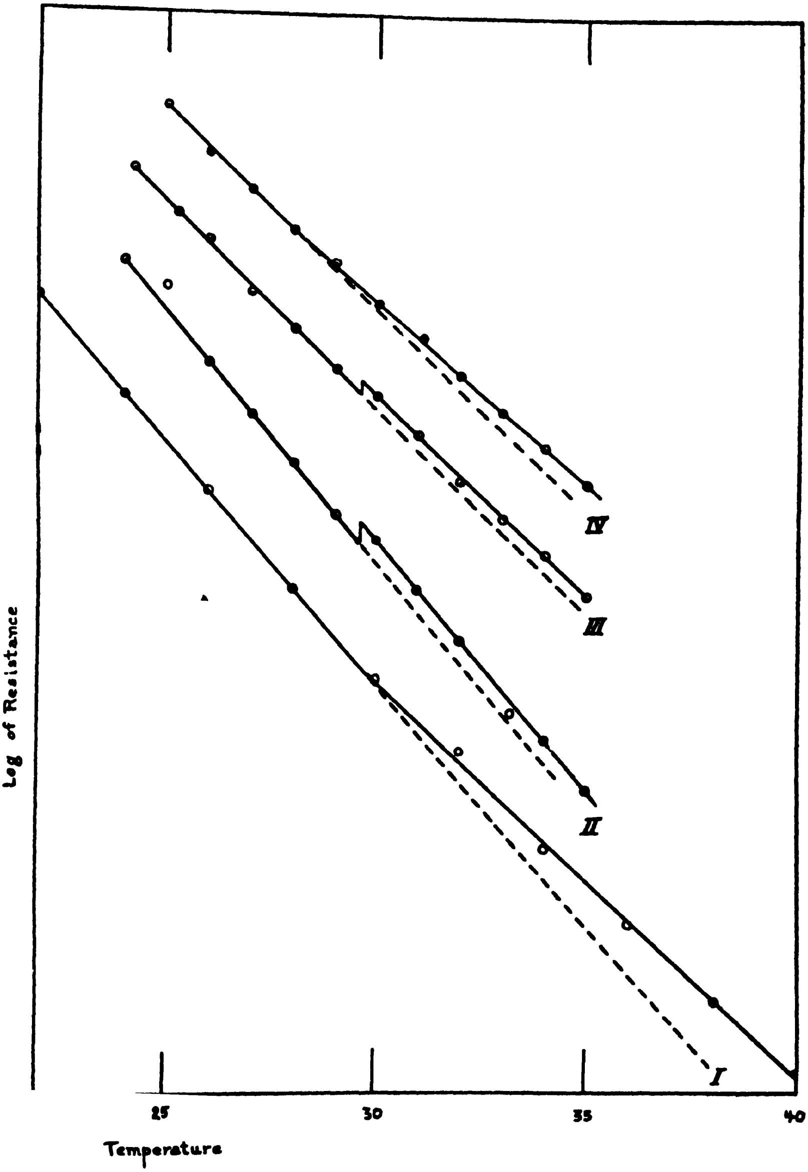

FIG. 1

abscissae. In both plots curves were obtained which approached straight lines in the neighborhood of the transition points. With the logarithmic plot the curves seemed to remain straight over a longer temperature range and so in the final plots and in the calculations the relationship between the temperature and the logarithm of the resistance was used. Such a plot of the data given in table 1 appears as figure 1, where the ordinates of the individual curves were adjusted in order to show several curves on a single plot. In each case smooth curves are drawn through the experimental points and the curve obtained below the transition point extended beyond this temperature as a broken line for emphasis. The value for the transition temperature calculated from the data obtained from solutions of lithium nitrate in pyridine agrees well with that found by Donnan and Butt (2) from solubility measurements, i.e., 29.6°C.

TABLE 2

$CdBr_2 \cdot 4H_2O = CdBr_2 \cdot H_2O + 3H_2O$ *in methyl alcohol (series 1), in ethyl alcohol (series 2)*
$Zn(NO_3)_2 \cdot 6H_2O = Zn(NO_3)_2 \cdot 3H_2O + 3H_2O$ *in methyl alcohol (series 3), in ethyl alcohol (series 4)*

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
26	62 87	28	556 2	28	113 2	28	196 5
28	61 61	30 5	546 2	30	112 3	30	192 6
30	60 50	32	538 6	32 2	111.4	32	188 8
32	59 41	34	530 0	34 2	110 5	34	185 5
34	58 22	36	522 6	36	110 1	36	182 1
36	57 29*	38	515 3	38	109 2	38 2	179 3
38	56 15	40	508 1	40	108 3	40	177 1
40	55 03*	42	501 1	42	107 5	42	174 7
42	54 16	44	495 1			44	172 2
44	53 19						
46	52 24						

The method of calculation as shown below depends upon the abrupt change in the slope of the resistance-temperature curve at the transition point, and the identity of the resistance at this temperature. The curves for lithium nitrate in acetone and in amyl alcohol (Curves II and III) are of interest even though they do not permit of the calculation of the transition point by the method here used. In both cases there is an abrupt change in the curve between 29°C. and 30°C., indicating the transition point between these temperatures, but the solvent medium and the number and nature of the conducting particles change in such a way as to make the temperature coefficient above and below the transition point almost identical. Thus in these two solvents parallel lines were obtained in each case in place of intersecting curves, making calculation of the exact transition point impossible. The last series in table 1 and Curve IV are based on the data obtained for solutions of calcium chloride in propyl alcohol. The value calculated for the transition point in this solvent is in fair agreement with that previously found for the salt in ethyl alcohol and with the value given by Bancroft (3) for the equilibrium temperature for the hexahydrate and the β-tetrahydrate.

TABLE 3

$ZnBr_2 \cdot 2H_2O = ZnBr_2 + 2H_2O$ *in pyridine (series 1)*

$CoCl_2 \cdot 6H_2O = CoCl_2 \cdot H_2O + 5H_2O$ *in glycol (series 2), in pyridine (series 3), in methyl alcohol at different concentrations (series 4, 5, and 6)*

SERIES 1		SERIES 2		SERIES 3	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
25	8982	25.1	788.2	20	22670
27.5	8766	26	762.6	22	22240
29	8660	27	738.1	24	21880
31	8487	28	714.4	26	21530
33	8334	29	691.5	28	21040
35	8184	30	666.8	30.5	20470
37.5	8021	31.1	648.3	32.5	20010
39	7925	32.1	627.7	34	19700
41	7768	33	610.3	36	19170
43	7675	34.1	591.1	38	18710
45	7553	35	574.7	40	18190
46	7493			42	17680

SERIES 4		SERIES 5		SERIES 6	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
24	336.3	24	78.19	24	32.54
25	334.3	25	77.54	25	32.22
26	330.9	26.1	77.06	26	31.96
27	329.6	27.1	76.58	27	31.70
28	327.6	28	75.95	28	31.51
29	325.6	29	75.48	29	31.32
30	323.6	30.1	74.86	30	31.07
31	321.7	31.1	74.40	31	30.82
32	319.1	32.1	74.10	32	30.58
33	317.8	33	73.79	33	30.44
34	315.9	34	73.49	34	30.27
35	314.0			35	30.08
				36	29.85

In table 2 are given the results obtained with cadmium bromide and with zinc nitrate, each in methyl and in ethyl alcohol. Solubility or other determinations leading to values of the transition point of an accuracy comparable to those used in the earlier paper for these and the remaining salts considered here do not seem to be available. In the previous work the average deviation from the established value of the transition found by this method using the above cell was about two-tenths of a degree. The emphasis in the present study, however, was placed upon extending the method to a larger number of solvents rather than establishing the exact values. The transition point of cadmium bromide according to Mellor (4) from consideration of the available data is 36°C. The value for zinc nitrate is given as about 35°C. Wasilieff (5) claims to have made a tetrahydrated salt and that it forms an eutectic with the hexahydrate at 35.4°C. Calculation of the data for this salt in ethyl alcohol gave 35.4°C. as the transition point; in methyl alcohol a curve was obtained similar to those for lithium nitrate in acetone and amyl alcohol.

In table 3 are given the data obtained from solutions of zinc bromide in pyridine and of cobalt chloride in ethylene glycol, in pyridine, and in methyl alcohol of various concentrations. The transition point of zinc bromide is given by Mellor (6) from consideration of solubility data as 35°C. According to a plot of the data compiled in Seidell (7), the transition point of cobalt chloride between the hexahydrate and monohydrate is at about 31°C. Landolt and Börnstein (8), on the other hand, indicate the transition point of the hexahydrate and dihydrate at about 50°C. and the possibility of a polymorphous transition of the hexahydrate between 30°C. and 35°C. Compilations of the solubility data for cobalt chloride in water show a curve which rises gradually as an almost straight line to about 30°C., at which point there is an abrupt curvature to about 50°C., where the line is cut by an almost straight line giving the solubility at higher temperatures. Corresponding with these points, the color of the solution changes from rose to violet and finally to blue. Numerous theories have been advanced to explain the changes in color and solubility, including equilibria of various salt hydrates, double salts, complex ions, and hydrated ions. The several viewpoints are summarized by Friend (9), who also mentions the change in color in aqueous salt solutions and in non-aqueous solvents.

In table 3 we have indicated the transformation as being that between the hexahydrate and the monohydrate, and calculation led to a transition temperature at about 31°C. The real change taking place at this temperature may be of quite a different nature and much more complicated. Whatever the cause, however, we found quite pronounced breaks in the resistance-temperature curves in all cases. The different solvents and concentrations gave different colored solutions, but in each case the break in the curve seemed to come at about the same point. The single exception was for the solution in glycol, where the calculated point was found to be 1.6°C. below that of the average in the four other solutions—in pyridine and in methyl alcohol. The deviation being so much greater than the average deviation would indicate an influence of the solvent rather than experimental error.

A single determination was made with this salt in the vicinity of 50°C., using ethylene glycol as solvent. A pronounced break was found in the curve at about 47°C. which again, owing to the solvent, may be lower than the true transition point for the change taking place at this higher temperature. In view of the findings given here it would appear that there is some abrupt change which takes place at about 31°C., and a further transformation at the higher temperature where the sharp change in the solubility curve is found.

TABLE 4

Calculation of transition points

SALT	SOLVENT	a	10^3b	a'	$10^3b'$	t	t'
Lithium nitrate	Pyridine	3 1255	−2 220	3 1145	−1 847	29 5	29 6
	Acetone					29-30	29 6
	Amyl alcohol					29 30	29 6
Calcium chloride	Propyl alcohol	2 6587	−6 190	2 6513	−5 932	28 7	29 2
Cadmium bromide[a]	Methyl alcohol	1 9054	−4 120	1 8986	−3 927	35 2	ca. 36
	Ethyl alcohol	2 8415	−3 433	2 8246	−2 960	35 7	ca. 36
Zinc nitrate	Methyl alcohol					34 2 36	ca. 35
	Ethyl alcohol	2 4108	−4 200	2 3692	−3 026	35 4	ca. 35
Zinc bromide	Pyridine	4 0542	−4 038	4 0346	−3 483	35 3	35 0
Cobalt chloride	Glycol	3 2632	−14 62	3 2162	−13 04	29 7	ca. 31
	Pyridine	4 4394	−4 162	4 4873	−5 690	31 3	ca. 31
	Methyl alcohol	2 5916	−2 721	2 5849	−2 510	31 8	ca. 31
	Methyl alcohol	1 9666	−3 063	1 9295	−1 860	30 8	ca. 31
	Methyl alcohol	1 5896	−3 252	1 5712	−2 663	31 2	ca. 31

CALCULATION OF THE TRANSITION POINT

As indicated above, the curves giving the relationship between the temperature and the resistance of solutions of salt hydrates in non-aqueous solvents approach straight lines at the transition points which in most cases intersect at this temperature. Equations giving the resistance as a function of the temperature may be developed, and since the resistance becomes identical at this point, the temperature may be calculated. In the present study it was found more advantageous to use the logarithm of the resistance, and equations for the two parts of the curve over the range where they appeared to be straight lines were calculated by the method of least squares in the form

$$\log R = a + bt$$

The results of such calculations are given in table 4. In the first and second columns are given the various salts and solvents. The constants *a* and *b*, given in the third and fourth columns, refer to the equation below the transition point and the values *a'* and *b'*, in the fifth and sixth columns, are for the corresponding curve above the transition point. Solution of the equations for *t* yields the values of the transition points given in the next to the last column. In the final column, under *t'*, appear such comparative data as can be found in the literature. In the tables above, all points obtained in the temperature interval are given. In the determination of the equations of the curves by this method, however, a few points may legitimately be omitted if from the plot they seem to be in error. This should be done particularly when such a point lies at or near the end of the curve and would thus, owing to the small number of points, have a considerable effect upon the slope of the curve and wipe out the self-consistency of the earlier points. This was found necessary in the present study only in the case of cadmium bromide, and the points omitted in the calculations are indicated in the table by asterisks; the remaining points in this curve and all of the points in the other curves were given equal weight. If from the graph a point appeared to be at the intersection of the lines it was included in the calculation of both curves. Obviously in order to achieve a high degree of accuracy with this method of determining the transition point, a larger number of points should be obtained for each branch of the curve so as to make the method of least squares truly significant.

SUMMARY

In the above study the transition points of a number of salt hydrates have been determined by observing the abrupt change of the resistance-temperature curves of solutions of these substances in several non-aqueous solvents. In most cases the numerical value of the point can be calculated, since merely a change in slope occurs at the point. Examples are also given, however, where the slope remains nearly constant, but the magnitude of the resistance changes abruptly. In all cases except for solutions of cobalt chloride in ethylene glycol the transition point was found to be independent of the solvent and, within the accuracy of the experiment, comparable with that found by other methods.

REFERENCES

(1) Lucasse and Harris: J. Phys. Chem. **30**, 930 (1926).
(2) Donnan and Butt: J. Chem. Soc. **83**, 335 (1903).
(3) Bancroft: The Phase Rule, p. 71. The Journal of Physical Chemistry, Ithaca, New York (1897).
(4) Mellor: Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume IV, p. 567. Longmans, Green and Company, New York (1923).

(5) Landolt-Börnstein Tabellen, Volume I, p. 687. J. Springer, Berlin (1923).
(6) Reference 4, p. 566.
(7) Seidell: Solubilities of Inorganic and Organic Substances, Volume I, p. 256. D. Van Nostrand Company, New York (1919).
(8) Reference 5, p. 648.
(9) Friend: A Textbook of Inorganic Chemistry, Volume IX, Part I, p. 39. J. B. Lippincott Company, Philadelphia (1920).

THE CHANGE IN THE TRANSFORMATION TEMPERATURE OF COPPER SULFATE AT 56°C. WITH THE SOLVENT MEDIUM

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Studies of the resistance of saturated solutions of copper sulfate in water have shown a break in the curve at about 56°C. (1). Electromotive force and solubility measurements have likewise indicated a change at about this point. In summarizing his data, Etard (2) gives two equations, one for the solubility at temperatures below 55°C. and another for that at higher temperatures. The change taking place at this temperature has been variously interpreted as a transition (3) from an α to a β pentahydrate and as the point of formation of $3CuSO_4 \cdot 4CuO \cdot 12H_2O$.

In the preceding paper, determinations of the transition points of salt hydrates have been given from a study of the resistance of solutions of constant concentration in several non-aqueous solvents. In all cases, except for solutions of cobalt chloride in ethylene glycol, the transition temperature was found to be the same within the experimental error as that given by other methods. In this system it was found that the break in the curve was about 1.6°C. below the transition point as indicated by other methods, or about four times the average deviation from the mean value found for this salt in other solvents. The transition temperature in general is lowered by the presence of foreign substances and different methods do not always yield the same value, but it was suggested that the effect in this case may have been due to the solvent. In the present paper are given results for the transformation of copper sulfate in glycerol-alcohol mixtures where the temperature is lowered several degrees.

The apparatus and method was entirely the same as in the previous paper. The results are given in table 1 where the resistances at various temperatures are given for solutions of copper sulfate in glycerol-alcohol mixtures of different proportions. The ethyl alcohol was purified and dehydrated as before. The copper sulfate and glycerol were of high quality and were not further purified. The solvent was made up by volume, seven parts of alcohol and three of glycerol, for example, being used for the 70 per cent alcohol solution. The solutions were prepared by shaking an excess of the pentahydrate with a quantity of the mixed solvent in an air-tight container. After settling, a portion of the supernatant liquid was transferred to the cell.

TABLE 1

The resistance of copper sulfate in glycerol-alcohol mixtures

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
42	4234	30	13500	42	2976	40	2226
44	3985	32	12180	44 2	2811	42	2120
46	3759	34	11130	46	2689	44	2012
48	3532	36	10150	48	2552	46	1913
50	3353	38	9256	50	2427	48	1816
52	3164	40	8408	52	2313	50	1734
54	3004	42	7698	54	2209*	52	1653
56	2845	44	7043	56	2097	54	1572
58	2700	46	6398	58	1998	56	1498
60	2561	48	5864	60	1908	58	1434
		50	5388			60	1374
		52	4975			62	1312
		54	4661				
		56	4314				
		58	4025				

SERIES 5		SERIES 6		SERIES 7		SERIES 8	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
36	5756	40 2	2546	42 2	15590	40	9577
38	5302	42	2397	44	14380	42	9124
40	4899	44	2230	46	13170	44	8699
42	4538	46	2092	48	11930	46	8333
44	4180	48 2	1946	49	11410	48 4	7887
46	3874	50 4	1814	50	10960	50	7658
48	3605	52	1732	52 2	9908	52	7330
50	3333	54	1623	54	9182	54	7019
52	3117	56	1536	55	8822	56	6765
54	2920	58	1444	56	8476	58	6494
56	2734	60	1365	58	7807	60 2	6236
58	2579					62	6038
60	2405					64	5823

In all cases, plots of the data obtained showed breaks in the curves at temperatures below 56°C. Constants for the equation

$$\log R = a + bt$$

for the portion below and above the break were calculated and the values of the transformation temperature calculated as in the previous paper. In table 2 the results are listed according to the increasing alcoholic content of the solvent. The series number given in the first column refers to the data in table 1 and gives the order in which the determinations were made.

TABLE 2

The transformation temperature of copper sulfate

SERIES	PER CENT ALCOHOL	a	10^2b	a'	$10^2b'$	t
7	20	5 0385	−2 002	4 9587	−1 841	49 6
2	30	4 7283	−2 004	4 5172	−1 576	49 3
5	50	4 3700	−1 698	4 2248	−1 405	49 6
6	60	3 9936	−1 463	3 9094	−1 292	49 2
1	70	4 1621	−1 276	4 1066	−1 164	49 6
3	80	3 9381	−1 106	3 9087	−1 048	50 7
4	80	3 7850	−1 094	3 7342	−0 9949	51 3
8	90	4 3649	−0 9635	4 2855	−0 8140	53 1

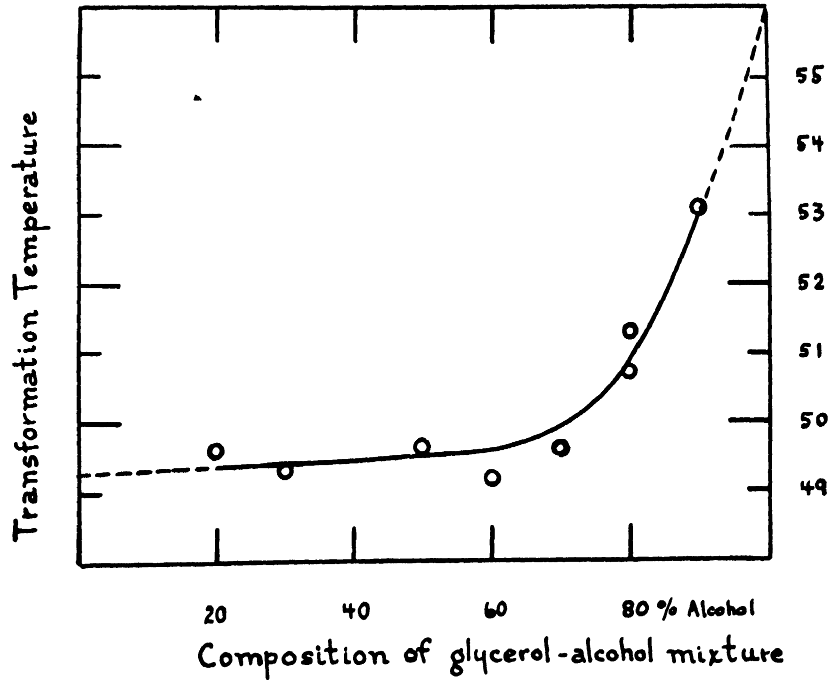

FIG. 1

The third and fourth columns give the values of the constants for the equation below the transformation temperature and the next two columns the corresponding values for the curve above this point. In the last column are listed the calculated transformation temperatures of the salt in the solvent of composition given in the second column.

A plot of these temperatures as a function of the alcoholic content of the solvent is given in figure 1, where the abscissae show the solvent composition and the ordinates the corresponding temperatures. Measurements in solutions of lower alcoholic content were difficult because of the high viscosity of the glycerol, and at higher concentrations because of the slight solubility of copper sulfate in alcohol. The smooth curve passing through the experimental points has been extended as a broken line in each direction to the pure components of the solvent.

The previous studies have shown that the transition points of the various salts used have been the same in solutions of ethyl alcohol as the values determined by other methods than the one used here, and the form of the curve with increasing alcoholic content makes it logical to extrapolate to 56°C. as the temperature at which the transformation would take place in this solvent, could sufficient amount be dissolved to determine the point. It is possible that at concentrations of glycerol greater than 80 per cent the curve again rises rapidly to 56°C. Should the curve be of that form, it would show the mutual lowering of the transition point by the added component of the solvent in each case. In the range measured, however, the curve shows no tendency to rise in the region of higher glycerol content. In view of the work with other solvents and with alcohol water mixtures, it seems unlikely, also, that traces of water or other impurities in the glycerol would lead to a constant depression in the material used. Nor does it seem likely that the form of the curve shown in the figure is due to any reaction or dehydrating effect of the glycerol. The measurements for series 1, 3, 5, and 7 were carried out as soon as the solutions were made up; those for 2, 6, and 8 about five hours after making the solutions; and for series 4 about forty-eight hours after.

It appears from this study, therefore, that copper sulfate undergoes a definite transformation at about 56°C. and that this temperature may be lowered by the solvent medium (4). As in all of the cases studied, since the solutions were saturated only at room temperatures, the break in the curve is due to a change in the system as a whole and not to the different temperature-solubility relationships of the two forms. Conclusions as to whether this change is between two forms of the pentahydrate or of a more complicated nature cannot be drawn, although it would seem that the formation of the compound indicated above would cause a more pronounced break in the temperature-resistance curve.

REFERENCES

(1) Cohen: Z physik. Chem. **31**, 164 (1899).

(2) Etard: Compt. rend. **104**, 1615 (1887); Ann. chim. phys. [7] **2**, 503 (1894). See however, Agde and Barkholt: Z. angew. Chem. **39**, 851 (1926).

(3) Landolt-Börnstein Tabellen, Volume I, p. 651. J. Springer, Berlin (1923).

(4) MacLeod-Brown: Chem. News **109**, 123 (1914).

PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. VI

THE PRESENCE OF FORMALDEHYDE IN RAIN WATER

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Since 1864, when Baeyer gave out his formaldehyde hypothesis, numerous attempts have been made to obtain formaldehyde *in vitro* from carbon dioxide and water on exposure to light. Usher and Priestley (1), Baly, Heilbron, and Barker (2), Dhar and coworkers (3), Mezzadroli and collaborators (4) and others obtained evidence of formaldehyde formation from carbonic acid or bicarbonates in presence or absence of catalysts, when exposed to light. On the other hand, Spoehr (5), Baur and Rebman (6), Porter and Ramsperger (7), Bell (8), Emerson (9), Zschiele (10) and Mackinney (11) obtained negative results, although the latter worker made the following statement:—"The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro*." Recently, Baly and coworkers (12) seem to contradict their earlier results.

It appears not only that the formation of formaldehyde is favored by radiations of short wavelengths, but also that a high light intensity is absolutely essential; some workers in this field could not obtain formaldehyde because of the low light intensity used.

In a recent communication, Dhar and Atma Ram (13) have been able to obtain larger yields of formaldehyde by the photoreduction of carbonic acid and bicarbonates by metals like magnesium, cerium etc.

It is well known that carbonic acid and water vapor exist in the atmosphere; under the influence of ultra-violet light from the sun, they should combine and form formaldehyde and oxygen. Hence, it seems probable that formaldehyde should be present in the atmosphere.

If appreciable amounts of formaldehyde were present in the atmosphere, formaldehyde should be partially washed down with rain water. In the last few months, in order to test whether formaldehyde occurs in rain water, we have analyzed numerous samples of freshly collected rain water obtained at Allahabad, Barlowganj (Mussoorie), altitude 5500 ft., and at a village 420 miles from Allahabad. In all cases we have got immediate and definite evidence of the existence of formaldehyde in both distilled and

TABLE 1

DATE	NUMBER OF HOURS AFTER WHICH THE SAMPLE WAS ANALYZED	AMOUNT OF FORMALDEHYDE PER LITER OF RAIN WATER *grams*	REMARKS
July 15, 1932	12	0.00075	After bright sunshine.
July 20, 1932	7	0.00082	After bright sunshine for 5 days.
July 21, 1932	4	0.0005	After a cloudy day.
July 26, 1932	Immediately	0 001	After 5 days of bright sunshine and clear sky.
July 26, 1932	12	0.0004	It had already rained 3 hours before.
July 27, 1932	Immediately	(1) 0.00082 (2) 0.0006 (3) 0.00045	After a bright day. Three different samples were collected one after the other.
July 28, 1932	Immediately	0 00045	It had rained the previous evening.
July 29, 1932	9	0.00052	After 9 hours of clear sunshine.
July 30, 1932	Immediately	(1) 0 00045 (2) 0.0004 (3) 0.0003	After a cloudy day. Three samples were collected one after the other.
July 31, 1932	5	0.0003	It had rained in the night.
July 31, 1932	Immediately	0.0003	Very slow rainfall.
July 31, 1932	8	0 00015	After a cloudy day. Rainfall throughout the whole night.
August 1, 1932	Immediately	(1) 0 00015 (2) Extremely small	Heavy rainfall for 3 hours.
August 2, 1932	4	0 00015	Occasional sunshine for 1 hour on the previous day.
August 3, 1932	Immediately	0 00025	After 4 hours of sunshine on the previous day.
August 3, 1932	Immediately	0 00025	Cloudy day. Heavy rainfall.
August 3, 1932	Immediately	0 00015	It had rained 3 hours before.
August 4, 1932	5	0 00015	Rained in the night.
August 4, 1932	Immediately	0 00022	Rained after sunshine for 2 hours.
August 5, 1932	Immediately	0 00022	Rained the previous evening.
	Immediately	0 0005	Bright sunshine throughout the day and rained in the evening.
	Immediately	0 00045	
	7	0 0003	
August 6, 1932	Immediately	0 0003	Rainfall in the night.
August 7, 1932	6	Absent	Heavy rainfall throughout the day and night.
August 7, 1932	Immediately	Absent	Heavy rainfall throughout the day and night.
August 7, 1932	Immediately	Absent	Heavy rainfall throughout the day and night.

TABLE 1—*Concluded*

DATE	NUMBER OF HOURS AFTER WHICH THE SAMPLE WAS ANALYZED	AMOUNT OF FORMALDEHYDE PER LITER OF RAIN WATER	REMARKS
		grams	
August 8, 1932	9	Absent	Cloudy the whole day.
August 9, 1932	Immediately	0.00045	After 5 hours of bright sunshine, it rained.
August 9, 1932	Immediately	(1) 0.0003 (2) 0.00015 (3) Very small	Cloudy. One of the heaviest rainfalls.
August 10, 1932	Immediately	0.00015	Cloudy the whole day and a very heavy rainfall the previous day.
August 12, 1932	4	0.00015	Cloudy on all the previous days.
August 15, 1932	Immediately	0.0004	Bright sunshine on the previous day.
August 16, 1932	Immediately	0.0003	Rained in the night.
August 17, 1932	Immediately	0.0003	Occasional sunshine for 2 hours. A heavy rainfall.

undistilled rain water, as tested by Schiff's reagent and Schryver's reagent, and by the reduction of ammoniacal silver nitrate.

In a recent note to Nature, it has been reported by us that formaldehyde occurs in freshly collected rain water. We have now estimated quantitatively the amounts of formaldehyde in rain water, and we have observed that the amount of formaldehyde in rain water increases if the shower is preceded by sunshine. When there is no sunshine between two showers the amount of formaldehyde is small, as will be clear from the results recorded below. Moreover, when rain water is analyzed immediately after the shower, the amount of formaldehyde is greater than when the rain water is analyzed after some time, because a part of the formaldehyde is lost by vaporization and another part undergoes polymerization (cf. Norrish and Kirkbride (14)).

The following experimental procedure was adopted: The rain water was collected in large porcelain dishes, placed on a tall stool in a clear space. Definite volumes of rain water were distilled and the distillate was analyzed for formaldehyde. An excess of standard $N/10$ solution of iodine was added to the distillate and 10 per cent sodium hydroxide solution till a permanent yellow color was developed. The reaction was allowed to proceed for about fifteen minutes, and then the mixture was acidified with strong hydrochloric acid to liberate the excess of iodine, and the iodine liberated was titrated against $N/100$ sodium thiosulfate solution. 1 cc. of $N/10$ iodine = 0.0015 gram of formaldehyde. The experimental results are given in table 1.

DISCUSSION

It is well known that hardly any radiation from the sun shorter than 2900 Å. is available on the earth's surface. It is generally believed that a very thin layer of ozone (3 mm. when reduced to 760 mm. pressure) formed in the atmosphere at higher altitudes is capable of absorbing solar radiation shorter than 2900 Å. This ozone is supposed to be formed by the absorption of shorter radiations by the oxygen of the atmosphere. In a recent communication, R. Mecke (15) has assumed that the photodecomposition of ozone by ultra-violet light with wavelengths shorter than 2655 Å. is a primary reaction, whilst the formation of ozone requires excited oxygen molecules and the efficiency of the photo-ozonization process can be raised by resonance effects. Thus, according to Mecke, the two primary photochemical reactions leading to an equilibrium are:—

$$O_3 + h\nu\ (\lambda < 2655\ \text{Å.}) = O_2' + O' \qquad (1)$$
$$O_2 + O_2\ (\lambda < 2025\ \text{Å}\ ) = O_3 + O' \qquad (2)$$

In each of these reactions excited oxygen atoms are supposed to be formed. Mecke has assumed the existence of several secondary reactions and has shown that at low pressure and small ozone concentrations, which are undoubtedly met with at high altitudes of the atmosphere, the law of equilibrium concentration is obeyed:—

$$3O_2 \rightleftarrows 2O_3$$

$$[O_3]^2/[O_2]^3 = K\ \text{(constant)}$$

From absorption measurements by various physicists, it is concluded that the mean altitude of the ozone layer in the atmosphere is about 50 kilometers and at this height the atmospheric pressure is about 10 ^{3} atmosphere. According to Fabry and Buisson (16), the total thickness of the ozone layer when reduced to normal pressure is 3 mm., i.e., 0.4 10 ^{6}, taking the height of the homogeneous atmosphere as a unit (7.99 kilometers).

From our experimental results, it is quite clear that formaldehyde also exists in the upper layers of the atmosphere, formed by the combination of carbon dioxide and water vapor in presence of the ultra-violet light of the sun. It is well known that the reaction

$$CO_2 + H_2O + 112\ \text{Cal.} = HCHO + O_2$$

requires ultra-violet light of wavelength approximately 2550 Å.

In recent years, Henri and Schou (17) and Herzberg (18) have measured the absorption spectrum of formaldehyde. They have observed that the absorption spectrum extends from 3700 Å. to 2500 Å. The spectum shows rotational fine structure down to 2750 Å., but between 2750 Å. and 2670

Å. predissociation begins which continues up to 2500 Å. The predissociation limit is shifted by 70 Å. towards the visible region when the temperature is elevated to 220°C. There are about 35 to 40 bands between 3700 Å. and 2500 Å. in the formaldehyde absorption spectrum. The maximum is at 2935 Å., characteristic of aldehydes. It is apparent, therefore, that not only does ozone absorb the short wavelengths from the sun, but the formaldehyde present in the atmosphere also absorbs the short rays of the solar radiations. Hence the absorption of the solar radiations shorter than 2900 Å., which has been attributed so far to the presence of ozone, may be partially due to the presence of formaldehyde. The maximum absorption of formaldehyde is at 2935 Å., but the maximum absorption of ozone appears to be at 2655 Å. Hence it seems that the ultra-violet rays filtered through the ozone layer may be absorbed by formaldehyde present in the atmosphere.

Water vapor is present in an appreciable amount in the atmosphere even at a height of 100 kilometers, but the amount of carbon dioxide present at the height of 40 kilometers is exceedingly small, less than 0.01 per cent. It appears therefore that formaldehyde in very small quantities may be formed nearly at the same height where ozone is photochemically generated in the atmosphere.

The dissociation energy of water is 110 Cal., whilst that of the oxygen molecule is 118 Cal. Hence it appears that the wavelength of the ultraviolet light capable of breaking up the O—H link may be slightly greater than that required to break the O=O link. When the O—H link is broken up, the carbon dioxide present in the atmosphere may be reduced to formaldehyde by the hydrogen atoms formed by the dissociation of water molecules. It seems that the atmospheric height at which formaldehyde is formed may be less than that where ozone is formed.

Just like ozone, formaldehyde is also photochemically decomposed. According to the recent experiments of Norrish and Kirkbride, the main products of the photodecomposition of formaldehyde are carbon monoxide and hydrogen. It is evident therefore, that the following equilibrium may

$$HCHO \rightleftarrows CO + H_2$$

exist in the atmosphere. It is well known that the upper atmosphere is rich in hydrogen. Consequently, owing to the presence of hydrogen in the upper atmosphere, the photodecomposition of formaldehyde will be markedly hindered, and appreciable amounts of formaldehyde can exist at an altitude of 40 to 50 kilometers or at lower altitudes. As water vapor exists in small quantities even at a height of 100 kilometers, the atmospheric formaldehyde may be washed down by the rain water. That is why all samples of rain water contain more or less formaldehyde. At the end of a very heavy shower, the amount of formaldehyde in the rain water becomes exceedingly small. At Barlowganj (U. P., India) which is situated at the height of 5500 ft. above the sea level, 8 inches of rain fell in five hours on the 12th of July, 1932, and at the end of the shower, some rain water was collected; the amount of formaldehyde in the freshly collected rain water was exceedingly small as tested by Schryver's reagent or by the reduction of ammoniacal silver nitrate solution.

In order that an appreciable amount of formaldehyde may be detected in rain water, the rain should be collected after some sunny days and should be analyzed as quickly as possible after the collection.

That the formaldehyde in the atmosphere is not generated from the decomposition of substances of vegetable origin on exposure to light is clear from the fact that hardly any formaldehyde is detected in the air near the land where there is plenty of vegetable matter. We passed several liters of air from an open space through 50 cc. of water placed in a stoppered flask for six hours, and on distilling the water no trace of formaldehyde was detected. It rained the same evening, when the above mentioned experiment was performed and the rain water collected contained an appreciable amount of formaldehyde.

It will be interesting to note that in a recent communication (19), it has been shown that there is evidence that the formaldehyde band is present in the solar atmosphere. It appears from spectroscopic evidence that formaldehyde, like cyanogen gas, may be present in the absorbing atmosphere of the sun.

Formaldehyde present in the atmosphere and rain water, even in small quantities, serves as a ready made food for plants. According to Sir J. C. Bose (20), in small doses, it serves as stimulant to the growth of plants. It can act as an antiseptic, can purify the air, and can act as a disinfectant to the soil.

SUMMARY

1. It has been observed that freshly collected rain water contains formaldehyde to the extent of 0.001 to 0.00015 g. per liter.

2. The amount of formaldehyde in rain water increases if the rain is preceded by bright sunny days. When the days are cloudy and there are frequent showers, the amount of formaldehyde decreases and may be altogether absent immediately after a very heavy shower.

3. The rain water should be immediately analyzed when collected, because a part of the formaldehyde is lost by vaporization and another part by polymerization.

4. It is believed that the formaldehyde in rain water is formed by the combination of carbon dioxide and water vapor present in the atmosphere by the absorption of ultra-violet light from the sun.

5. Formaldehyde in rain water cannot be due to the photodecomposition of substances of vegetable origin.

6. Formaldehyde vapor shows light absorption between 3700 and 2500 Å., the maximum absorption being at 2935 Å., characteristic of aldehydes. It appears that not only does ozone absorb radiations of short wavelengths from the sun, but also the formaldehyde present in the atmosphere absorbs solar ultra-violet radiations.

7. It appears that the water molecules are decomposed by absorption of short wave radiations and the hydrogen atoms set free reduce carbon dioxide to formaldehyde, which may be formed in the atmosphere at heights less than those where ozone is generated.

REFERENCES

(1) Usher and Priestley: Proc. Roy. Soc. London **B84**, 101 (1911).
(2) Baly, Heilbron, and Barker: J. Chem Soc. **119**, 1025 (1921).
(3) Dhar and coworkers: J. Phys. Chem. **29**, 926 (1925); **35**, 1418 (1931); **36**, 567 (1932).
(4) Mezzadroli and collaborators: Atti accad. Lincei **6**, 160 (1927); Gazz. chim. ital. **59**, 305 (1929).
(5) Spoehr: J. Am. Chem. Soc. **45**, 1184 (1923).
(6) Baur and Rehman. Helv. Chim. Acta **5**, 928 (1922).
(7) Porter and Ramsperger: J. Am. Chem Soc. **47**, 79 (1925).
(8) Bell: Trans. Faraday Soc. **27**, 771 (1931).
(9) Emerson: J. Gen. Physiol. **13**, 163 (1929).
(10) Zscheile: J. Am. Chem. Soc. **54**, 973 (1932).
(11) Mackinney: J. Am. Chem Soc. **54**, 1688 (1932).
(12) Baly and coworkers: Proc. Roy. Soc. London **A116**, 212 (1927).
(13) Dhar and Ram: Nature **129**, 205 (1932); Z. anorg. allgem. Chem. **206**, 171 (1932).
(14) Norrish and Kirkbride: J. Chem. Soc. **1932**, 1518.
(15) Mecke, R.: Trans. Faraday Soc. **27**, 375 (1931), Discussion on photochemical processes.
(16) Fabry and Buisson: J. phys. **3**, 163 (1913).
(17) Henri and Schou: Z. Physik **49**, 744 (1928).
(18) Herzberg: Trans. Faraday Soc. **27**, 378 (1931).
(19) Dhar: Z. anorg. allgem. Chem. **206**, 270 (1932).
(20) Bose: Physiology of Photosynthesis, p. 71. Longmans, Green and Company, New York (1924).

COMMUNICATIONS TO THE EDITOR

THE DECOMPOSITION OF OZONE BY ALPHA PARTICLES AND BY THERMAL MEANS[1]

I should like to report the results of experiments carried out one and a half years ago with W. Feitknecht in this laboratory on the decomposition of pure ozone by alpha particles from radon at room temperatures. The *M/N* ratio, the number of molecules decomposed per ion pair, was found to be high, varying from about 4,500 at 50 mm. ozone to about 15,000 at 300 mm. ozone. The rate of decomposition followed the equation

$$-\frac{d[O_3]}{dt} = \frac{dp}{dt} = K[O_3]^n$$

where for a series of runs n was found to be 1.5. Very good constants were obtained throughout a given run and the constant was the same for different pressures. The rate was independent of the presence of oxygen. The *M/N* ratio was found to be proportional to $[O_3]^{2/3}$. Since ionization by alpha particles is practically proportional to the pressure in the range investigated, this makes the rate of decomposition proportional to $[O_3]^{1.67}$, in substantial agreement with the rate found. It is thus seen that rather long chains are possible in ozone decomposing at room temperatures. These facts provide evidence in favor of the viewpoint of Riesenfeld and Wassmuth (Z. physik. Chem. 8B, 314 (1930)), but not that of Schumacher and Sprenger (Z. physik. Chem. 6B, 446 (1930)). These experiments are to be extended and will be reported on later.

More recently, during a study of the kinetics of the explosion of ozone induced by hydrogen, a rather complete series of experiments on the thermal decomposition of pure ozone was made at 85°C. between initial ozone pressures of 40 to 200 mm. and in different glass and quartz vessels. The rate of decomposition is represented by the equation

$$-\frac{d[O_3]}{dt} = \frac{dp}{dt} = K[O_3]^{1.5}$$

K remains constant down to 80 per cent decomposition, which is as far as the reaction was carried usually. *K* seems to depend on the initial concentration, for it increases somewhat as the latter is raised. In a given run the rate is independent of the oxygen concentration, but K is higher for an initial mixture containing ozone plus oxygen than for a similar amount of ozone alone.

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On investigating the published results on this subject of Schumacher and Sprenger (loc. cit.), who employed a 5-liter cylindrical vessel, Riesenfeld and Wassmuth (Z. physik. Chem. **143,** 408 (1929)), and Riesenfeld and Bonholtzer (Z. physik. Chem. **130,** 255 (1927)), it is found that their experiments also are represented very well by the same relationship. When corrections are made for the temperature, using the known temperature coefficient, and when allowance is made for the initial pressure, the rate constants of their experiments derived from the above relationship agree quite well with the present ones. These authors have explained their rates by supposing that a monomolecular and bimolecular reaction are occurring simultaneously despite the fact that their corrected "true" monomolecular and bimolecular constants change with initial pressure (particularly the monomolecular constants, see Z. Physik. Chem. **143,** 408 (1929)).

All the experiments are now in agreement and may be assumed to be correct. The interpretation yet remains. It seems more natural for the reaction to be represented by a simple formula rather than to introduce unnecessary complications of simultaneously occurring monomolecular and bimolecular reactions. The 1.5 power indicates that the reaction is to be explained by a chain mechanism, just as in the alpha ray experiments. What this mechanism is will be left for a future publication.

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THE ADSORPTION OF RADON BY SILICA GEL

In view of the work of Francis (Kolloid-Z. **59,** 292 (1932)) on the adsorption of radon by silica gel, certain measurements of ours, made under widely different conditions, should be of interest. Our measurements were made by a static method, using comparatively large amounts of radon; the pressure of the other gases present was very low, not more than four or five times that of the radon itself. The silica gel used in these experiments was a clear glassy gel which had been purified by treatment with concentrated nitric acid. It was then dried in a stream of air at about 300°C., and finally electrodialyzed for a long period of time. Before use it was dried once more at 300°C. The gel contained about 5 per cent of water.

In one experiment, 34 millicuries of radon were left in a glass tube, which contained 1 g. of silica gel, for twenty-four hours. The portion of the tube containing the silica gel was then sealed off from the rest, and the radon contents of both tubes were determined by means of a gamma ray electroscope. Allowing for the free space in the tube which contained the gel, the distribution coefficient (radon per gram of gel divided by the radon per cubic centimeter of free space) was found to be 144. This lies between the highest value (44) observed by Francis for an aged gel, and the highest value (335) for a freshly prepared gel. In his experiments a flow system was used and equilibrium was reached between the gel and a very small amount of radon mixed with air at atmospheric pressure.

In a second experiment about 100 millicuries of radon was allowed to distribute itself between 1 g. of silica gel at room temperature and a tube (of about 5 cc. capacity) which was immersed in liquid air. At equilibrium 43 per cent of the radon was found to be adsorbed on the gel. This indicates a surprisingly large difference in the adsorptive capacity of silica gel and (Pyrex) glass for an inert gas.

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NEW BOOKS

Report on Band-Spectra of Diatomic Molecules. By W. Jevons, D.Sc. 26 x 18 cm.; viii + 308 pp. London: The Physical Society, 1932. Price: (paper covers) 17s. 6d. net; (in cloth) 20s. 6d.

It is difficult to rate this book too highly. The author has devoted some three years to its preparation, and remarkable clarity of exposition and care for detail are maintained throughout, betraying no signs of any desire to hasten a conclusion. This is praiseworthy in view of the rapid development of the mechanical significance of band-spectra, and it is indicative that such a lengthy report can be written from the "observational, rather than the purely theoretical, aspect of the subject." We may take this as signifying that the fundamental principles are so firmly established that the "theoretical results necessary for the interpretation of the analyses of bands and band-systems" may be "briefly stated, with no indication of the quantum-mechanical methods used in their derivation." This is now possible, whilst only a few years ago textbooks on spectroscopy essentially dismissed the whole of band-spectra with a casual reference to their probable association with molecules.

The report, in the words of the author, is "mainly addressed to the physicist who has not hitherto taken up band-spectra as a subject for special reading or laboratory work;" in the opinion of the reviewer the author should have made wider claims, since the larger proportion of chemists are unfamiliar with the modern interpretations of the fundamental principles of their science by mathematical physicists. Here is an opportunity for the chemist to see how the spatial and thermal properties of molecules are rigorously defined by spectroscopy, how conceptions of valency are being altered and extended, and how the excitation of individual molecules as a necessary preliminary to chemical reaction is bound up with alterations in their detailed electronic structure, the conditions and consequences of such alterations being well on the way to spectroscopic determination. In short, we may be nearing the time predicted by Mulliken when the advance of mathematical technique is such that it may be easier to calculate the properties of polyatomic molecules than to determine them experimentally.

It is to be emphasized that however clear, logical, and fluent the presentation of the results and conclusions in spectroscopic work may be—and the present report is a model in that respect—no benefit is likely to be derived from casual reading. This is due partly to the complexity and all-embracing nature of the subject, and partly to the extensive notation required, and the author does well to insist upon frequent reference to the valuable glossary offered in Appendix I. Mulliken's notation as used, although it has produced order out of chaos, has rendered more complicated some of the simpler expressions familiar to spectroscopists, and may need further revision when our knowledge of the band-spectra of polyatomic molecules approaches a similar finality.

Certain matter, generally of a descriptive nature, has been relegated to small type, with the suggestion that it might be omitted by the "more casual reader," but if this process is applied to Chapter V, dealing in a most able and concise way with line-spectra and the electronic states of atoms, this reader will find the remaining half of the book largely unintelligible. Nothing but praise is to be found for the typography of the Cambridge Press, and for the sixty-four diagrams, all of which seem to have been specially prepared by the author for the report.

It is hardly possible to select any portion of the book for individual praise, but the chapter on the isotope effect is well done, and represents the first reasonably complete account of the phenomenon. As an indication of how far the references are up-to-date, one may cite the identification of H^2 (page 211), and the isotopes of germanium (page 227). The most valuable feature from the point of view of those already working in the field of band-spectra lies in the table of constants for electronic states and band-systems given in Appendix II. The foreword to the Appendix should be consulted for an appreciation of the possibilities offered by the data provided, and although any approach to completeness is disclaimed, it is difficult to see what purpose would be served by any further search of the literature by those interested.

The time is scarcely ripe for a similar report dealing with the theoretical significance of the observed results, and the author has probably done wisely in attempting no discussion of such problems as valency. The stress on the observational aspect leads to the dismissal of the phenomenon of predissociation in two pages, and one can but wait with great interest for the eventual appearance of a companion volume. The work as it stands is a magnificent achievement, and the highest praise is due to the successful collaboration of the author, printers, and publishers.

C. R. Bailey.

The Method of Dimensions. By Prof. A. W. Porter, F.R.S. 17 x 11 cm.; v + 80 pp. London: Methuen and Company, 1933. Price: 2/6.

In this volume, one of the recent additions to Methuen's series of short monographs on physical subjects, Professor Porter has collected together important applications of the method of dimensions. The more fundamental and still controversial subject of units has up to the present time had the greater attention, and the author has done well to bring to our notice the existence of a very useful tool. It is important however that the student should realize the limitations of the method· it should be used only when other methods of approach have failed to give an understanding of the physics of the problem. A little greater emphasis on this aspect of the subject, together with a rather more extended introductory treatment of units, would perhaps have increased the value of the book, particularly for the physical chemist. A historical introduction stressing the fundamental work of Newton, and, later, of Fourier, leads the way to discussion of such problems as the time of swing of a simple pendulum, the flow of fluids, surface tension, and heat effects. A final section deals with electromagnetic and electrostatic units. Many references to original papers and summary articles are given and one or two blank pages at the end are available for notes. The present writer had hoped to see, from the point of view of historical interest, some reference to Einstein's early application of the method of dimensions to the determination of the frequency of vibration of atoms in a solid body. This is not, however, to detract from the large amount of useful information which Professor Porter has set before us, and the book will be of considerable value to all students of physics and physical chemistry.

J. T. Randall.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 30: Barium. 26 x 18 cm.; xviii + xvi + 390 pp. Berlin: Verlag Chemie G. m. b. H., 1932. Price: 64 M. (subscription price 56 M.).

This volume gives a very complete account of the chemistry of barium and its compounds and is complete in itself. There are thirty-one figures in the text. The literature references are thoroughly covered and no doubt practically all have been seen in the original, as in previous volumes of the work. The mineralogy and geology of barium and the physical properties of the element and its compounds are fully dealt with and the literature includes the year 1932. The book is indispensable both to chemists and physicists and maintains the high standard of previous volumes.

J. R. PARTINGTON.

Structure Symbols of Organic Compounds. By INGO W. D. HACKH. viii + 139 pp. Philadelphia, P. Blakiston's Son and Co. Price: $2.50.

The author has devised an ingenious set of shorthand symbols for organic compounds, which he advocates as a substitute for—or rather, improvement on—the ordinary structural or graphic formulas using the chemical symbols of the elements and the usual connecting bonds.

As a teaching device, the reviewer doubts very much if these symbols would have the value claimed for them, namely, that they make it possible to include a larger amount of organic chemistry in the usual courses; and it would appear that the new symbols might have the definite disadvantage of getting the student even further away from reality than the usual structural formulas do, since in the new symbols no symbols for carbon, hydrogen, nitrogen, or oxygen appear.

But as a tool for advanced students and research workers, these new symbols appear highly advantageous, for they amount to a shorthand way of representing the structural formulas and can be written in much less time than even the most abbreviated structural formulas. This, it seems to the reviewer, is the field in which these symbols have their greatest advantage, and this advantage is a considerable one.

The first thirty-five pages of the book are given over to a discussion of the formulas, and then follow twenty-nine plates showing the formulas for about a thousand typical organic compounds. There is an index.

LEE IRVIN SMITH.

Einführung in die Tonphotographie. Photographische Grundlagen der Lichttonaufzeichnung. By J. EGGERT AND R. SCHMIDT. 23 x 15.5 cm.; vi + 137 pp. Leipzig: S. Hirzel, 1932. Price RM. 7. Card covers.

The ear is far less tolerant in judging the reproduction of sound than the eye in judging the scale of intensities in a monochrome photograph. The difficulties encountered in reproducing sound free from distortion are therefore very considerable, and it is partly for this reason that so much experimental work has been carried out to investigate the photographic technique of sound recording. Few people could be found who are in better position to write an explanatory book on this difficult subject than Professor Eggert and Dr. Schmidt. They have been working in this field for some years and have now produced an excellent little book which should be welcomed by all interested in the general problems of photographic sensitometry as well as by those engaged more narrowly in the actual problems of sound-recording. The book is well printed on good paper; there are one hundred and twenty-two very good illustrations, together with literature and general indexes.

S. O. RAWLING.

Handbuch der Spectroscopie. Band VIII, Lieferung 1. By H. KAYSER and H. KONEN. 26 x 18 cm.; iv + 654 pp. Leipzig: S. Hirzel, 1932. Price RM.67.50.

It is now thirty-two years since the first volume of Kayser's Handbuch was published, and it is interesting to read today in the preface to that volume the scheme Professor Kayser had in mind for the complete work. The fourth volume was to contain the complete account of the emission spectra of each element, with a supplementary volume on experimental methods. He hoped to add a fifth volume to include astrophysical spectroscopy. We signal today the publication of the first part of an eighth volume, which is to be devoted entirely to the emission spectra of the elements. The phenomenal advance in knowledge of emission spectra, which has given rise to the continued expansion of this great treatise, occasions a reflective mood. Whilst one may legitimately wonder what may possibly be the state of knowledge of the spectra of the elements described in the final section of this volume, compared with that of those now dealt with, one cannot but hold up to admiration the devoted labors of Professor Kayser and Professor Konen and of their six collaborators, which have given to the scientific world a book so urgently needed.

The present volume deals with the spectra of the elements from silver to copper, arranged as previously in the alphabetical order of their symbols. In general, the series terms and individual lines have been expressed in the modern notation, but this has in some cases been impossible. Difficulties arose from the want of agreement amongst authors in the use of the modern system, and also from the want of consistency in its use by individual authors. A conversion to the modern notation was at times found to be impossible without a re-investigation of the whole spectrum, which would have involved much time and indeed does not lie within the purview of a book which aims at a faithful presentation of published work. In these cases the original notation used by the author has been given.

It must be remembered that the present volume is part of a supplementary volume to those already published. Thus in the tables of wave-lengths only those measurements are included which have been published since Volume VII was written. Furthermore, the literature references for each element are numbered consecutively to those given for that element in Volume VII. In general, therefore Volume VIII should be used in conjunction with Volumes V to VII.

Under each element the line and band spectra are dealt with, the latter also as measured in the absorption spectra of such compounds as have been examined. The emission spectra are extended into the very short wave-length region of the x-rays. The measurements of the Zeeman and Stark effects are included of all lines which have been examined, and the Raman effect is also added. As may be readily appreciated, the latter measurements are given only where they stand in immediate relation to the simpler spectra, the broader application to organic compounds being omitted. Lastly there are to be found the measurements of fluorescence and reasonance spectra so far as these have been studied.

In assessing the value of this new volume, an excerpt from the authors' preface may be quoted as a text. If, they say, there be found some want of uniformity as the result of the collaboration, we believe that this will be far outweighed by the advantage gained both from the more rapid continuation of the work and from the fact that the collaborators are experts in different sections, whilst in these days a single individual can scarcely gain an equal mastery of the whole. As specialization in spectroscopy becomes more narrow, so is one the more pleased to have at hand a well coördinated and admirably compiled account of the whole field of emission spectra. The literature of the subject is much enriched by its publication.

C. C. C. Baly.

Das Rhenium. By Dr. W. Schröter, with an introduction by Dr. W. Noddack. 25.5 cm. x 16.5 cm.; pp. 59. Stuttgart: Ferdinand Enke, 1932. Price: RM. 5.50.

Though we welcome this account of the earlier chemistry of rhenium it is, we feel, published at an unlucky moment. Since rhenium became available commercially a number of workers have so extended our knowledge of the element that some parts of the book, and those not unimportant, are already out of date and misleading. While much of the book is very useful and illuminating, the reader, unfortunately, cannot be quite sure, especially about the simple chemistry of rhenium, without checking it by the original publications of the last two years or so or by the excellent account given in the recently published volume of "Mellor."

The extraction of rhenium from various minerals, particularly molybdenite, and its subsequent purification are fully described, but the brief account of its technical production carefully refrains from any indication of the actual source of the element.

Much interesting information is given about metallic rhenium but the description of its compounds needs correction, even in a review. There is no sure evidence of hexavalent rhenium or of the rhenates indicated on pages 12 and 39. The existence of Re_2O_8, described at length on pages 32 and 33 has been disproved. No mention is made of the very characteristic and interesting pentoxide, Re_2O_5. Rhenium hepatachloride and hexachloride, which are described (page 39), do not exist; while the very characteristic volatile, black, crystalline tetrachloride, the main product of the action of chlorine on the metal, is not even mentioned (pages 40 to 42). Another serious omission is that of the equally characteristic and interesting volatile, stable oxychlorides, $ReOCl_4$ and ReO_3Cl.

The book concludes with a section on the occurrence of rhenium and tables which show very clearly how insignificant that occurrence is except in certain varieties of molybdenite from Norway and Japan. A bibliography of the literature of rhenium is given from its discovery in 1925 to 1931, but this, as has been indicated, omits recent work including some papers published in 1931.

Applied X-rays. By G. L. CLARK. Second edition (first edition, 1927). pp. 470. New York: McGraw-Hill Book Co., 1932. Price: $5.00.

The growth of the application of x-ray science to a study of material structures is remarkably demonstrated by a comparison of the two editions. The new volume is about 200 pages longer than the first. The first part of the later edition deals with the fundamental physics of x-rays, use of x-ray spectra in chemical analysis, and description of modern equipment. Chapter 3, dealing with x-ray tubes, is an excellent feature of the book. A variety of high grade tubes for the various uses, radiography, deep therapy, crystal analyses, and chemical analysis, is now available and these are clearly described. Anyone planning to select equipment will find this chapter very useful. The following chapter on high tension equipment also contains much useful information.

The second half of the book describes the standard methods of x-ray analysis of crystals, but does not list the line-extinctions corresponding to the different space groups. For this purpose, recourse must be made to tables by Wyckoff or other workers. Then follows an excellent summary of the results of crystal analyses of inorganic compounds, and of alloys, giving due attention to the excellent contributions to crystal chemistry by Goldschmidt and Westgren. One chapter is devoted to carbon compounds with descriptions of the work in laboratories of Sir William Bragg and of Trillat. A good deal of attention is given to the study of the condition of solids as regards grain-size, orientation, internal strain and mechanical deformation. This branch of x-ray science will undoubtedly be extended more and more in the near future. The effects of drawing wire and rolling sheet metal on crystal orientation and on physical properties are already a subject of much interest.

The last chapter is devoted to high polymers, such as rayon, cotton, rubber, and human muscle. Many studies of stretching fibers are reported and illustrated with excellent photographs. The new high-intensity x-ray tubes permitting very short exposures will prove useful in this field.

The book forms part of the International Series in Physics, edited by F. K. Richtmyer. It should prove a useful part of the working library of all investigators in x-ray science.

N. W. Taylor.

ADHESION TENSION

PRESSURE OF DISPLACEMENT METHOD

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Received March 23, 1933

Preliminary papers describing a pressure of displacement method for the measurement of adhesion tension were first published from this laboratory in 1927 (1). At that time the method used was new; it was time-consuming and required much patience and exactness of technique. Calculations were dependent upon the use of contact angle values, which values were of necessity obtained in the course of the investigation and by indirect methods. Certain fundamental assumptions were made which, though apparently justified, had not been subjected to rigorous experimental tests. Although there was no reason to believe that the results were seriously in error, publication of the major part of them was withheld until portions of the work had been rechecked and the soundness of each individual step of the method more definitely established.

As one step in the determination of contact angles, the pore radii of compressed powder membranes were determined by the pressure of displacement method. Comparison of results obtained with this method and with a method based upon application of Poiseuille's law showed close agreement (2). This fact tended to justify the use of the pressure of displacement method for the measurement of pore radii.

The angle of contact formed between certain liquids and a solid in the presence of air, and of certain liquid-liquid systems in contact with solid, were determined by different methods. Values obtained for liquid systems in transparent single capillary tubes (3) in which measurements were made directly by a photomicrographic method, were in good agreement with those obtained by the pressure of displacement method.

Adhesion tension, A_{12}, has been defined as the difference between the surface tension of solid, S_1, and the interfacial tension of this solid, S_{12}, in contact with a given liquid, i.e.,

$$A_{12} = S_1 - S_{12}$$

There has been some question as to whether the indirect pressure of displacement method will actually give a true measure of the value $S_1 - S_{12}$. In this method as developed it was necessary to measure interfacial contact angles, θ_{23}, of organic liquid and water in contact with each other against a solid. In some of the systems studied by us there must have been an appreciable mutual solubility of the organic liquid and water. It was not known to what extent this mutual solubility would invalidate the final results. The free surface energy values of the interfacial systems (solid-air and solid-liquid) should be numerically equal to the interfacial tension values of these systems and the symbols, S_1 and S_{12}, have been used also in referring to free surface energy values. When used to represent free surface energy values, the expression $S_1 - S_{12}$ should represent the energy of immersion, i.e., should represent the free surface energy change which occurs when the solid substance is immersed within the liquid.

To test this point an investigation was undertaken in which the energy of immersion of a solid (silica) was determined for a series of organic liquids (4). It was found that energies of immersion thus obtained show good agreement with those calculated from data obtained with the pressure of displacement method. It thus appears that the adhesion tension value of a given solid-liquid system (i.e., for the systems studied) as determined by the pressure of displacement method is numerically equal (or at least very nearly equal) to the free surface energy change which occurs when the solid is immersed in the liquid.

Every step of the pressure of displacement method has been checked by at least one different and independent method and in every case the results obtained have been found to be in agreement. It appears, therefore, that all assumptions which were made in connection with the pressure of displacement method were justified. Accordingly we feel that we can now release data which have been accumulated over a period of years. In the present paper will be presented the data obtained in the preliminary work (i.e., prior to 1927), and in later papers will be given data obtained in more recent researches. Much of the latter work has been done with materials of a high degree of purity and with such improvements in method as have developed as the work has progressed.

PRELIMINARY EXPERIMENTS

Some of our first experiments on relative wetting of solids by liquids were made by means of the method of Reinders (5) and of Hofman (6). Solids used were carbon black, ultramarine blue, and Prussian blue. Liquids used were water and different organic liquids. About equal quantities of water and of organic liquid were put into a test tube with a small amount of the finely divided solid and shaken. It was noted that carbon went exclusively to the organic liquid phase and ultramarine blue to the water phase, while Prussian blue failed to show a decided selective wetting tendency. If the Prussian blue powder were first wetted by water it tended to remain in the water phase; if first wetted by organic liquid it was then not readily wetted by water, but in either case a fairly large proportion of it tended to remain finally at the water-organic liquid interface. This method was useful in obtaining qualitative evidence on relative degrees of wetting of different solid-liquid systems, but no quantitative relationships could be obtained with it.

DISPLACEMENT OF ONE LIQUID BY ANOTHER FROM A SOLID

It occurred to us that instead of observing to which liquid phase the solid particles would go, it might be to advantage to reverse the procedure and by working with a comparatively large amount of solid, as a compact membrane, to determine in which direction the liquids would move. It was believed that data obtained should give information concerning the interfacial tension relationships of the system, and hence information concerning relative degrees of wetting.

If a diaphragm be prepared by firmly packing a finely powdered solid, it forms a membrane containing a large number of fine capillary pores; membranes of this type have previously been employed for the measurement of osmotic pressures (7, 8)

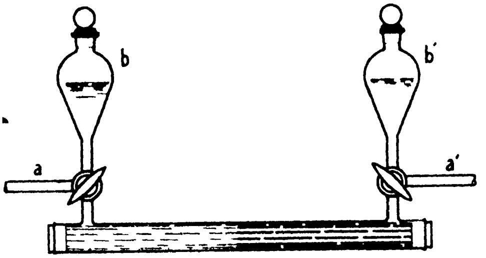

FIG. 1 APPARATUS FOR LIQUID DISPLACEMENT

From the theory of capillary action it may be concluded that a liquid will not pass through such fine capillary pores unless it first wets the pore walls, but that, if the liquid does wet the pore walls, it will travel through the pores and so-called capillary action will occur. In case two liquid columns are in contact within such pores, other factors being equal, that liquid giving the higher interfacial tension against the solid will be displaced by the other liquid.

The first apparatus used by us for liquid displacement is represented in figure 1.

It consisted of a glass tube 3 sq. cm. in cross-section and 20 cm. in length provided with three-way stopcocks, with outlet tubes, *a* and *a′*, and glass reservoirs, *b* and *b′*, mounted near the ends. Pigment wetted by one of the liquids was packed into the tube to the half-way mark, and pigment wetted with the other liquid was packed against this until the tube was filled, after which stoppers were inserted in the ends of the tube. In this way two thick membranes were obtained, each wetted by a liquid, the two liquids being immiscible and in contact. In case of liquid displacement the direction and the amount of displacement could be determined by noting the change in length of the liquid columns in the outlet tubes. Any loss of liquid by leakage or by evaporation could be detected by comparing the movement in one capillary tube with that in the other.

The initial results obtained are shown in table 1. Fairly good checks were obtained in a series of experiments with each of these systems. When Prussian blue was used as solid there was practically no movement of the liquid column in either direction. The results were all in good agreement with those obtained in the test tube experiments mentioned above. The apparatus can be easily constructed and is suitable for qualitative measurements.

Various types of apparatus were next tried, but for lack of space will not be described.

TABLE 1

NO	SOLID PHASE	LIQUID A	DISPLACES LIQUID B	IN 5 HOURS
1	Powdered glass	Water	Benzene	100 cm.
2	Powdered glass	Water	Turpentine	8 cm.
3	Carbon black	Benzene	Water	60 cm.
4	Carbon black	Turpentine	Water	45 cm.
5	Ultramarine blue	Water	Turpentine	20 cm.
6	Ultramarine blue	Water	Benzene	70 cm.
7	Ultramarine blue	Water	Kerosene	36 cm.

DEVELOPMENT OF METHOD AND APPARATUS FOR DETERMINATION OF DISPLACEMENT PRESSURES

The displacement cell used in the main investigation herein described is shown in figure 2.

The cell consisted of a cylindrical tube of brass, into which the powdered solid could be firmly compressed. This was accomplished by means of tightly fitting perforated plungers.[1] A fine-mesh cloth disc was placed over the powder to prevent escape through the perforations. After compression of powder the plungers were firmly secured in place by means of steel yokes, bolts, and nuts. The apparatus was made leak-proof by employing rubber, leather, or lead gaskets, which were held tightly in place by screwing down a threaded nut and gasket. Glass capillary tubes were fastened securely into the outer ends of the plungers. One of these tubes was fastened by means of a ground glass joint to a pressure gauge or manometer. The other tube served as a displacement indicator. Movement of liquid within the cell was detected by movement of the meniscus of the liquid in this (capillary) tube.

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[1] In practice special packing plungers are used. In construction they are similar to the plungers herein described.

The solid to be studied was reduced to a fine powder. Best results were obtained by grading this powder to a uniform particle size (200 mesh to 300 mesh is highly satisfactory). This powder, dry or thoroughly wetted by liquid as the case might demand, was packed in about 1-g. increments in the manometer end of the cell by means of a laboratory hydraulic press. A packing pressure of approximately 150 atmospheres was used. After the cell was about three-fourths full, the solid material wetted by the displacing liquid was then added and compressed. While the cell was still in the press and under pressure, the plungers were secured in place by the steel yokes and bolts. The apparatus, when assembled, was found to withstand internal pressures as high as 100 atmospheres without exhibiting leaks.

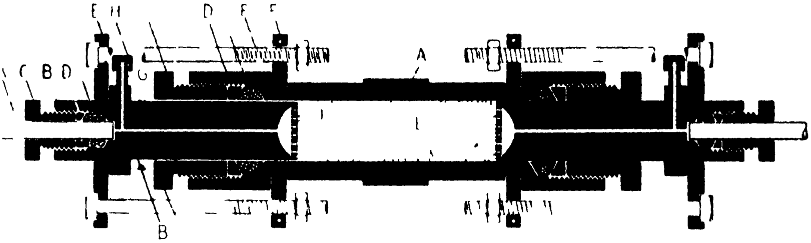

FIG 2 DISPLACEMENT CELL

A, cell casing; B, plungers; C, packing gland; D, packing ring; E and E′, steel yoke; F, steel bolts; G, outlet tube; H, cap; I, packing material; J, perforated plate; K, glass capillary; L, powdered solid.

METHOD OF OBTAINING DISPLACEMENT PRESSURES

After the cell had been properly filled with wetted powder it was quickly attached to the indicator tube and manometer. Air pressures were set up of such magnitude as to prevent an appreciable movement of liquid within the cell. As the liquid tended to move, the opposing pressure was increased. In this way the pressure was built up to the maximum value necessary to prevent any advance of liquid. This operation usually required a number of hours. Sometimes twenty-four to thirty-six hours elapsed before it could be concluded that maximum or equilibrium pressure had been reached. Each of the pressure values recorded is an average of a number of independent runs. It often required a number of days to obtain one properly checked pressure of displacement value. Pressure values obtained by a series of runs for any given system usually checked to within less than 1 per cent.[2]

MATERIAL USED

The carbon used was a Germantown lampblack. It was treated with ether to remove greasy material, then dried and heated for a short time to approximately 1200°C. It was finally evacuated at less than 10^{-4} mm. pressure for sixty to seventy hours and wetted with the required liquid while still under vacuum. The silica was technical "Tripoli" which was treated with hydrochloric acid, thoroughly washed with water, dried and heated in a muffle furnace to approximately 1200°C. Analysis gave 99.15 per cent silica. It should be pointed out that all results recorded for a given solid were obtained from a single batch of solid material. The liquids were of average C. P. grade and were not highly purified. It was thought that in this initial work an attempt to use highly purified materials was not justified.

RESULTS

The results obtained with silica and with carbon black are given in table 2.

The effective pore radius, r, was calculated from displacement pressures of benzene-air and was found to be 2.1×10^{-4} cm. for silica and 9.3×10^{-5} cm. for carbon.

The adhesion tension of α-bromonaphthalene against silica, A_{12}, was found to be 41.92, and of water against silica, A_{13}, 81.5 dynes per centimeter The adhesion tension of water against carbon, A_{13}, was found to be 54.74 dynes per centimeter. With these adhesion tension values for water against the two solids, the adhesion tension values of the other liquids could be determined (provided the values of the interfacial contact angles θ_{23} were known) since the values of their interfacial tension, S_{23}, could be obtained from the literature. The following equation is applicable:

$$A_{13} = A_{12} + S_{23} \cos \theta_{23} \text{ (for silica)}$$

In their work on liquid absorption, Bartell and Hershberger (9) made the observation that "the order of decrease in the free surface energies which occur when a polar solid is wetted by each of a series of zero contact angle liquids is the same as the order of decrease in free surface energies which occur when water is brought into contact with this same series of liquids."

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[2] In a recent article (Davis and Curtis: Ind. Eng. Chem. **24**, 1137 (1932)) describing the use of this method in another laboratory, it was pointed out that "results have been checked with the same briquettes within about 5 per cent and with different briquettes within about 8 per cent maximum variation for a given liquid." These results can mean only that the method as used in that laboratory was not under proper control for accurate work.

In view of this generalization the liquids given in table 2 are placed in the order of progressive decrease in free surface energy exhibited when they are brought into contact with water. This order is likewise the order of decreasing interfacial tension values (column 3) of the organic liquid-water systems. It is interesting to note that this order is, with few exceptions, the order found for increasing adhesion tension values, A_{12}, for silica (column 7).

TABLE 2

Adhesion tension data

Organic liquids against carbon and against silica

			CARBON $r = 9\ 5 \times 10^{-6}$ cm A_{12} (for water) = 54 74		SILICA $r = 2\ 1 \times 10^{-4}$ A_{12} (for water) = 81 5 A_{12} (for α-bromonaphthalene) = 41 92	
	S_2	S_{21}	θ_{13}	A_{12}	θ_{23}	A_{12}
Carbon disulfide	31 3	48 1	41°35′	90 77	37°10′	43 2
Carbon tetrachloride	26 1	44 5	44°45′	86 38	19°00′	39 5
α-Bromonaphthalene	44 0	41 6	35°03′	88 81	13°30′	41 1
Toluene	28 1	36 1	40°40′	82 10	38°50′	53 4
Benzene	28 3	34 6	40°30′	81 03	28°40′	51 2
Chloroform	26 5	31 6	37°25′	79 83	43°40′	58 7
"Decalin"	31 0	26 7	35°45′	76 38		
Nitrobenzene	43 3	25 3	11°00′	79 58	37°30′	61 4
"Tetralin"	32 8	22 4	11°35′	76 70		
Butyl acetate	24 1	13 2	33°00′	65 78	44°40′	72 1
Ethyl carbonate	25 8	12 4	29°25′	65 55		
Amyl acetate	24 4	10 9	34°40′	63 68	44°45′	73 7
Ether	16 5	10 7	61°30′	59 85		
Propyl acetate	23 8	9 6	29°15′	63 09	42°55′	74 4
Ethyl acetate	23 4	6 8	50°20′	59 07	37°10′	76 1
Aniline	42 5	5 7	15°45′	60 22	82°05′	73 8
Amyl alcohol	23 7	5 0	35°25′	58 77	37°45′	77 5
Benzyl alcohol	39 4	4 8	32°50′	58 73		
Isobutyl alcohol	22 4	1 8	0°00′	56 60	5°45′	80 7

It is also to be noted that the order of a series of liquids showing increasing adhesion tension values against silica is just the reverse of the order showing increasing adhesion values against carbon. Liquids giving the highest adhesion tension values against silica give the lowest adhesion tension values against carbon and vice versa.

It is further to be noted that for each one of this series of liquids the sum of the adhesion tension values of liquid against carbon and against silica is practically a constant. This is a striking fact, and will probably lead to an important generalization. It is felt, however, that further information should be obtained before an explanation is attempted. Data with other solid-liquid systems are now being obtained in the hope that an obvious and valid generalization may be deduced.

WORK OF ADHESION

When the liquids are arranged in groups representing similar chemical constitution, consideration of the different work of adhesion values brings out interesting relationships when the different work of adhesion values are considered (table 3). The work of adhesion values, expressed by the equation,

$$W_a = S_1 + S_2 - S_{12}, \text{ or } W_a = A_{12} + S_2$$

are, for the different members of a given group (liquids of similar constitution), of very nearly the same magnitude when considered for a given system, i.e., for either carbon, silica, or water.

TABLE 3

Work of adhesion of a series of liquids against carbon, silica and water

	CARBON W_a	SILICA W_a	WATER W_a
Benzene	109 3	79 4	65 7
Toluene	110 2	81 5	64 1
Nitrobenzene.	122 8	104 7	90 1
Aniline	102 7	117 2	108 9
α-Bromonaphthalene .	132 8	85 1	74 5
Tetralin	109 5		82 5
Decalin	107 4		76 4
Chloroform	106 2	85 2	67 0
Carbon tetrachloride	112 4	65 6	53 7
Carbon bisulfide ..	122 1	74 5	55 3
Ethyl acetate	82 5	99 5	88 7
Propyl acetate	86 8	98 1	86 3
Amyl acetate	88 1	98 0	85 6
Butyl acetate	89 8	96 2	84 0
Amyl alcohol	82 5	101 2	90 8
Isobutyl alcohol	79 0	103 1	92 7
Ethyl carbonate	91 4		85 5
Ethyl ether	76 4		77 9
Water	126 8	153 6	144 16 ($= W_c$)

The work of adhesion values of benzene and of toluene against carbon are practically the same. The values for these two liquids against silica are similar, and the values against water are likewise very nearly the same. The other aromatic compounds give high work of adhesion values against carbon. Aniline and nitrobenzene give relatively high values, both against silica and against water. This is probably due to the effect of the polar group. Chloroform, carbon tetrachloride, and carbon disulfide give high values against carbon, but considerably lower values against both silica and water. The alcohols give slightly higher values against silica than do the acetates. When the work of adhesion values are considered from the standpoint of molecular orientation the results are in approximately the order one would expect.

It has been pointed out earlier in the paper that no high degree of purity is claimed for the liquids used and that the characteristics of the solids cannot be accurately described. In later investigations it has been found that the adhesional properties of carbon can be altered, and that these properties are dependent upon the precise treatment to which the carbon has been subjected (10). But little was known of the structure of the silica used in this investigation since it was "purified" technical "Tripoli." In subsequent investigations carried out in our laboratories fused quartz, analyzed white sand, and other forms of comparatively pure silica have been used. With these latter materials the adhesion tension values have been somewhat lower (in some cases 6 dynes lower) than those obtained with the "Tripoli." The adhesion tension values for water against these pure silicas were found to range from 76 to 79.5, as compared with the value 81.5 found in this investigation. Inasmuch as all the other values determined are dependent upon the water-silica value, the values for the other liquids are correspondingly lower in the later work. At the time the work herein reported was carried out, only one liquid forming a contact angle against silica was used, namely, α-bromonaphthalene. In later work a number of other liquids have been used and have been found to give values which are in agreement. Recent work with α-bromonaphthalene has shown that contact angle values obtained with it are dependent largely upon the precise nature and manner of treatment of the silica surface (11). The data herein presented are reasonably accurate for the surfaces used, however, and since they may prove to be of considerable practical value, should be made available. Much time must elapse before the exact degree of accuracy of the values can be definitely determined, but when used in the light of relative values they are certainly significant

SUMMARY

1. An account is given of the preliminary work carried out in the development of methods for the determination of adhesion tension data.

2. The pressure of displacement method for the measurement of adhesion tension is described in considerable detail.

3. Adhesion tension values and work of adhesion values obtained with a series of liquids against silica and against carbon are given.

REFERENCES

(1) Bartell and Osterhof: Ind. Eng. Chem. **19**, 1277 (1927). Fifth Colloid Symposium Monograph, p. 113. The Chemical Catalog Co., Inc., New York (1927).
(2) Bartell and Osterhof: J. Phys. Chem. **32**, 1553 (1929).
(3) Bartell and Merrill: J. Phys. Chem. **36**, 1178 (1932).
(4) Bartell and Almy: J. Phys. Chem. **34**, 985 (1932).
(5) Reinders: Kolloid-Z. **13**, 235 (1913)
(6) Hofman: Z. physik. Chem. **83**, 385 (1913).
(7) Bigelow and Robinson: J. Phys. Chem. **22**, 99 (1918).
(8) Bartell and Osterhof: Fourth Colloid Symposium Monograph, p. 230. The Chemical Catalog Co., Inc., New York (1926).
(9) Bartell and Hershberger: Ind. Eng. Chem. **22**, 1304 (1930).
(10) Bartell and Smith: Ind. Eng. Chem. **21**, 1102 (1929).
(11) Bartell and Wooley: Unpublished observations.

MIGRATION STUDIES WITH COLLOIDS. I

THE EFFECT OF ELECTROLYTES AND OF COLLOIDS OF OPPOSITE SIGN ON THE STABILITY OF COLLOIDAL SYSTEMS

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A. THE EFFECT OF ELECTROLYTES ON THE STABILITY OF COLLOIDAL SYSTEMS

INTRODUCTION

It is well known that addition of electrolytes to lyophobic colloids, whose prime factor of stability is an electric potential originating in the Helmholtz double layer, results in a decrease in the stability of the dispersed particles. When sufficient electrolyte is added the decrease in stability is manifested by coagulation of the sol. Schulze (1) long ago found that electrolytes with polyvalent ions were the better coagulators. This generalization is modified (2), however, by the adsorbabilities of the ions.

Hardy (3), while studying the cataphoresis of denatured egg albumen, concluded that coagulation resulted only when there was no migration of the particles in an electric field. Powis (4), however, has shown in the case of hydrophobic colloids that it is not necessary to reduce the particles to an isoelectric condition in order to produce coagulation.

Since there thus appears to be a definite relationship between the rate of cataphoresis and colloidal stability, migration data may be used as a measure of the stability of sols, assuming that these measurements are proportional to the stabilizing potential. It is to be emphasized that velocity determinations offer a means of following changes in the stability of suspensoids before coagulation takes place. An ultramicroscopic technique was employed in the present investigation. This method affords a high degree of accuracy in measuring cataphoresis and in addition presents the unique opportunity of obtaining reliable velocity measurements after coagulation has taken place.

The data submitted in Part A are on a group of sols which were used in the mutual coagulation study reported in the following paper.

PREPARATION OF SOLS

The following sols were used: positive arsenic trisulfide, iron oxide, aluminum oxide, chromium oxide, and negative iron oxide, stannic oxide, manganese dioxide, arsenic trisulfide.

Attempts were made to prepare the positive arsenic trisulfide sol by recharging a negative sol with thorium nitrate solution. However, these efforts were unsatisfactory in that considerable precipitation of arsenic trisulfide always resulted regardless of the method of mixing. Subsequently it was found that if a solution of arsenious oxide was added to a dilute solution of thorium nitrate and hydrogen sulfide passed into this mixture, a stable positive sol was formed. The sol was then washed with hydrogen.

The positive iron oxide sol was prepared by hydrolysis of ferric chloride in boiling water and then purified by dialysis for a week at 70–90°C. The negative iron oxide sol was obtained by adding an equal volume of a dilute potassium ferrocyanide solution to a portion of the positive sol. It required only 0.025 millimol of the electrolyte per liter to produce a stable negative colloid.

The other colloids were made by standard methods. The sols were dialyzed in collodion sacks to reduce the presence of electrolytes to a minimum.

EXPERIMENTAL

The cataphoresis determinations were carried out by a method previously described (5).

Samples of sol for observation with the ultramicroscope were prepared by diluting the original stock colloids. The amount of dilution was determined by the "visibility" of the particles. It was desired to employ the maximum concentration of colloid that would permit the observation of a single particle with the means at hand. In this manner it was possible to obtain reliable coagulation data along with the velocity measurements. The systems on which data are given were made by mixing 25 cc. of electrolyte solution with an equal volume of sol. The samples were run approximately one-half hour after mixing. The time necessary for a particle to traverse 200 μ was recorded. Ten readings were taken in alternate directions using a potential of 91.5 volts between electrodes 11.5 cm. apart. The mean was selected for calculation of the velocity.

After the velocity determinations had been made the samples were set aside for twenty-four hours. Observations for coagulation were then made.[1]

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[1] In the interests of space economy, migration and coagulation data are not presented in tabular form. Migration data are represented graphically. Coagulation data may also be interpolated from the graphs since, within close limits, the sols coagulated when the velocity of the particles had been reduced to $\pm 2.0\ \mu$ per second per volt per centimeter

RESULTS

The order of anions in reducing the migration velocity of the aluminum oxide sol is $Fe(CN)_6 > PO_4 > CrO_4 > SO_4 > Cl$. The same order is maintained with positive iron oxide. Figures 1 and 2 show graphically the behavior of the two sols with electrolytes. The data with chromium oxide are plotted in figure 3. A different order of the anions is encountered with this sol, i.e., $CrO_4 > SO_4 > PO_4 > Cl$. The position of the ferrocyanide ion in the lyotropic series was not determined. For concentrations up to 0.016 millimol per liter the tetravalent ion had no more effect in discharging the chromium oxide particles than the phosphate ion. Increasing the concentration of potassium ferrocyanide past 0.016 millimol per liter led to the formation of a gelatinous precipitate which clogged the cataphoresis cell and made working conditions impossible.

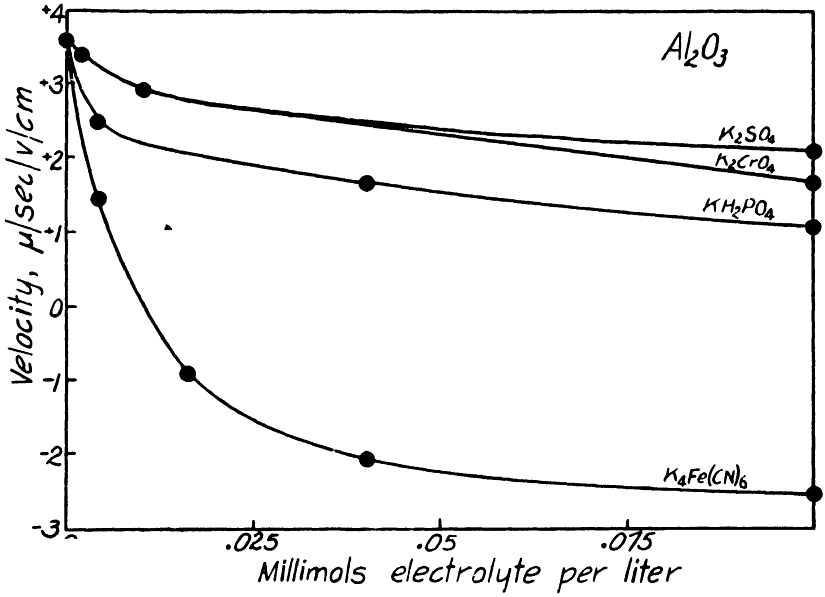

FIG. 1

Figure 4 brings out the following order of anions with positive arsenious sulfide: $Fe(CN)_6 > SO_4 > PO_4 > CrO_4 > Cl$. The position of the sulfate ion is questionable, since at low concentrations it is not as effective as phosphate. The striking thing about figure 4 is the potassium chromate curve. It does not seem probable that the potassium ion would charge the micelle in the presence of the bivalent chromate ion. A faint greenish opalescence had been noted in the samples containing potassium chromate. This suggested a reduction to chromic ion by the hydrogen sulfide incompletely removed when the sol was washed with hydrogen. To test this

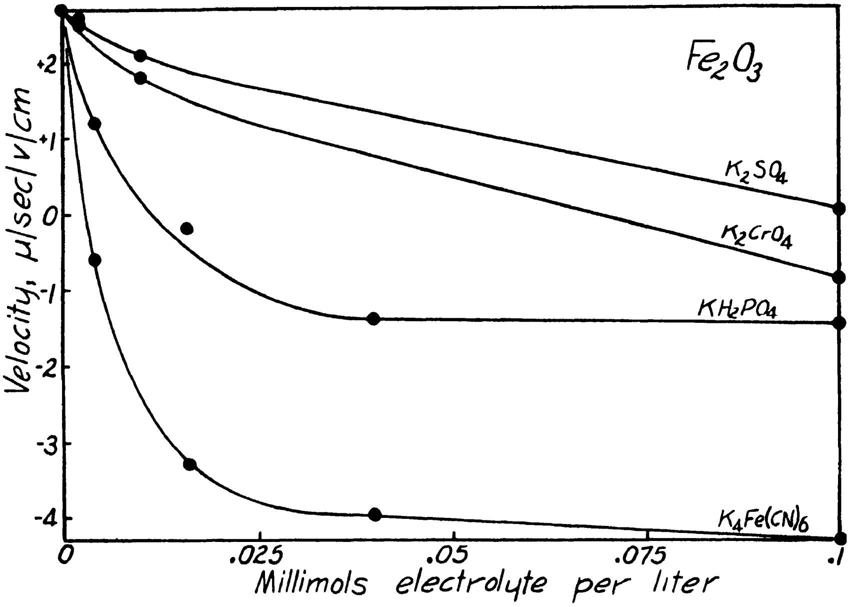
Fe2O3
K2SO4
K2CrO4
KH2PO4
K4Fe(CN)6
Velocity, μ/sec/v/cm
+2
+1
0
-1
-2
-3
-4
0
.025
.05
.075
.1
Millimols electrolyte per liter

FIG. 2

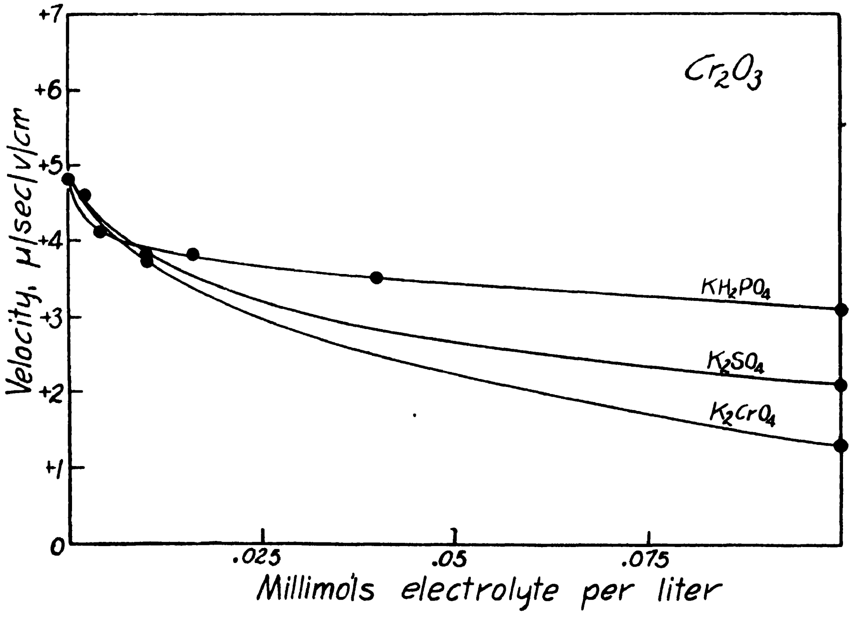
Cr2O3
KH2PO4
K2SO4
K2CrO4
Velocity, μ/sec/v/cm
+7
+6
+5
+4
+3
+2
+1
0
.025
.05
.075
Millimols electrolyte per liter

FIG. 3

point potassium chromate was added to a negative arsenic trisulfide sol until the mixture contained 0.1 millimol of the electrolyte per liter. The migration velocity of the negative sol was reduced from -3.4 to -1.0 μ per second per volt per centimeter and the sol coagulated. This indicates strongly that the anomalous behavior of chromate with positive arsenic trisulfide can be explained by the reduction of the bivalent negative ion to chromic ion. The results with the negative arsenic trisulfide sol and potassium chromate were probably due to failure to remove all of the unadsorbed hydrogen sulfide during the process of washing with hydrogen. If it be assumed that adsorbed hydrogen sulfide is not free to act as a reducing agent, then the behavior of an arsenic trisulfide sol[1] with chromate ion should give an indication of its purity. One is in a quandary when removing the hydrogen sulfide from an arsenic trisulfide sol, because if the washing is carried out too far the arsenic trisulfide hydrolyzes.

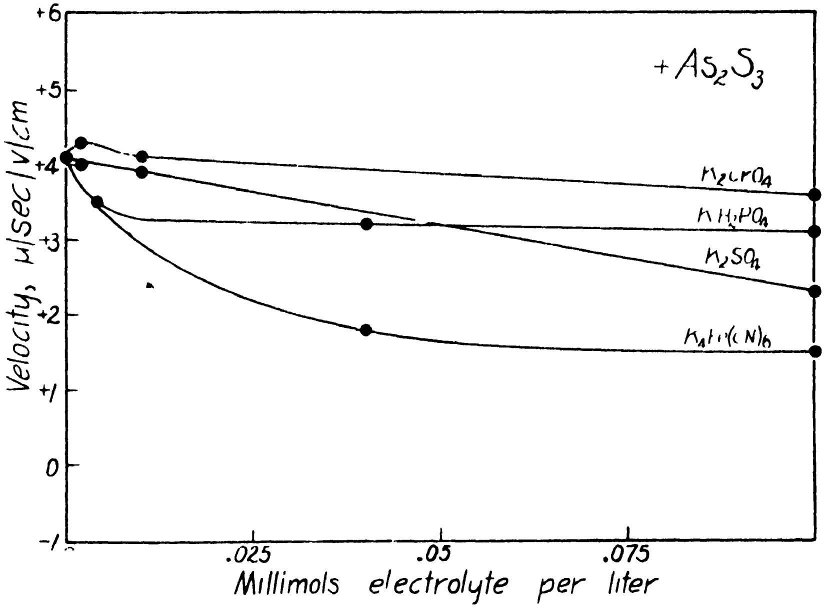

FIG. 4

The data with negative sols and electrolytes are plotted in figures 5 to 8. From figure 5 the order of cations with arsenious sulfide is Th > Cr > Al > Fe > Ba > K at low concentrations, with aluminum and iron exchanging places at higher concentrations. The stannic oxide curves in figure 6 give Th > Al > Cr > Fe > Ba > K for the order of ions at the lower concentrations, with the order changed to Al, Th > Ba > Cr > Fe > K at the highest concentration studied. The order of cations with man-

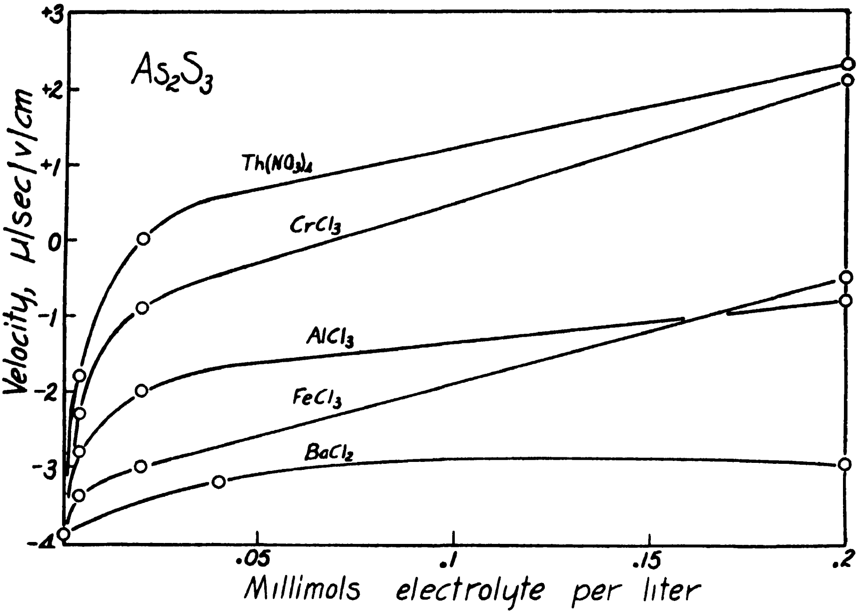
As_2S_3
Velocity, μ/sec/v/cm
+3
+2
+1
0
-1
-2
-3
-4
$Th(NO_3)_4$
$CrCl_3$
$AlCl_3$
$FeCl_3$
$BaCl_2$
.05
.1
.15
.2
Millimols electrolyte per liter

FIG. 5

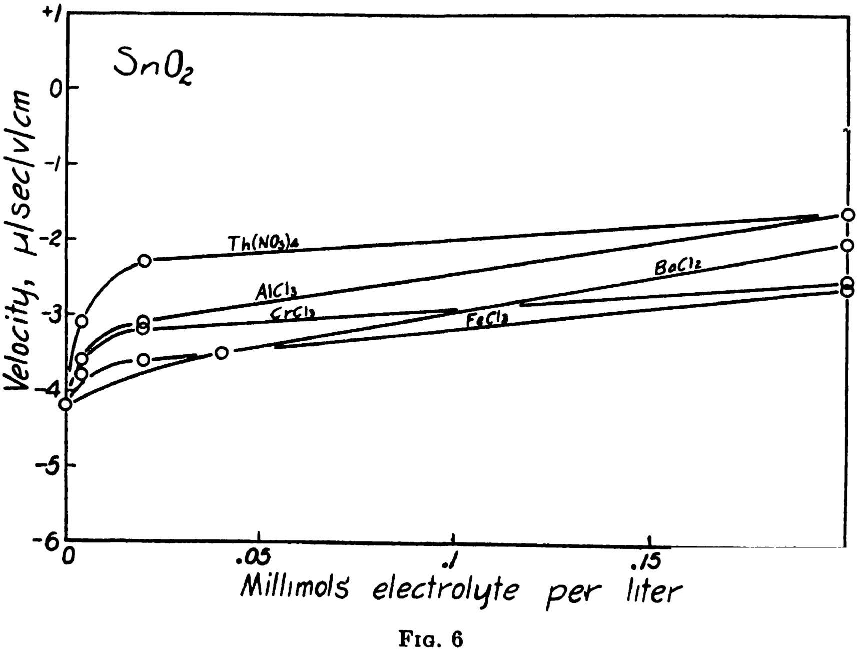
SnO_2
Velocity, μ/sec/v/cm
+1
0
-1
-2
-3
-4
-5
-6
$Th(NO_3)_4$
$AlCl_3$
$CrCl_3$
$FeCl_3$
$BaCl_2$
0
.05
.1
.15
Millimols electrolyte per liter

FIG. 6

ganese dioxide is Th > Al > Cr, Fe > Ba > K but this is altered to Th > Cr, Fe > Al > Ba > K when 0.2 millimol per liter of the electrolytes is present. Figure 8 with negative iron oxide indicates that Th > Cr > Al > Fe > Ba > K is the order of effectiveness of cations in decreasing the mobility of the particles.

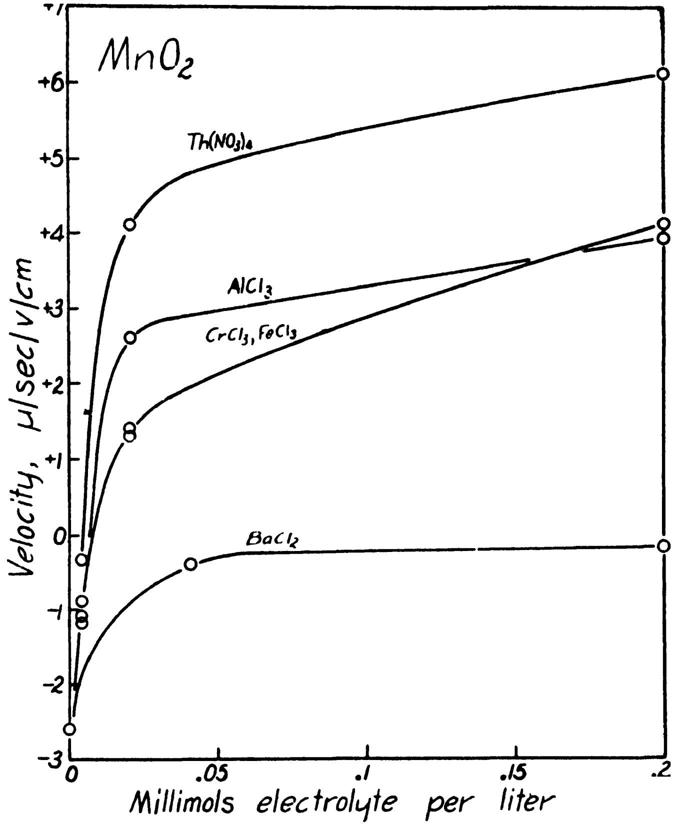

FIG. 7

If we are to assume that there is a relationship between migration velocity and stability, the above orders of ions might serve as lyotropic series.

Some of the salts used were considerably hydrolyzed, as evidenced by the following pH values determined with a glass electrode.[2] The data are for $M/1000$ solutions.

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[2] The pH data were kindly supplied by Mr. Herbert Ellison.

Electrolyte	*pH*
$AlCl_3$.	3 6
$CrCl_3$	2 8
$FeCl_3$	2 3
$Th(NO_3)_4$	2.7

It is evident that the amount of free acid varies with the electrolytes. Therefore it was thought of interest to investigate the effect of the hydrogen

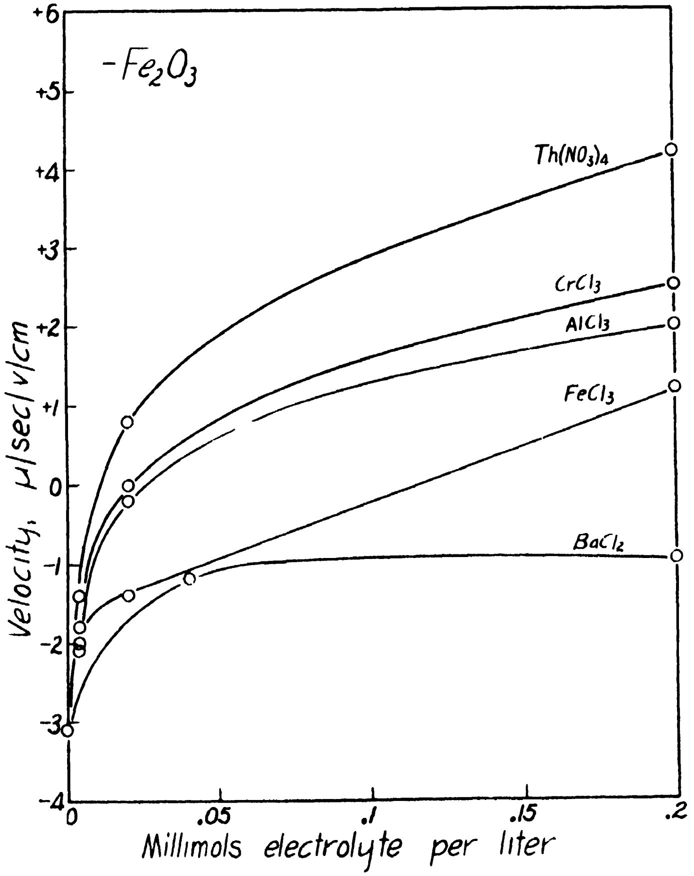

FIG 8

ion on the migration velocity of the sols. Figure 9 shows the behavior of negative sols with hydrochloric acid. Hydrochloric acid exhibits a strong, antagonistic, charging action with the arsenic trisulfide sol. At low concentrations the acid is quite inactive in discharging the tin oxide particles, but it is very effective at higher concentrations.

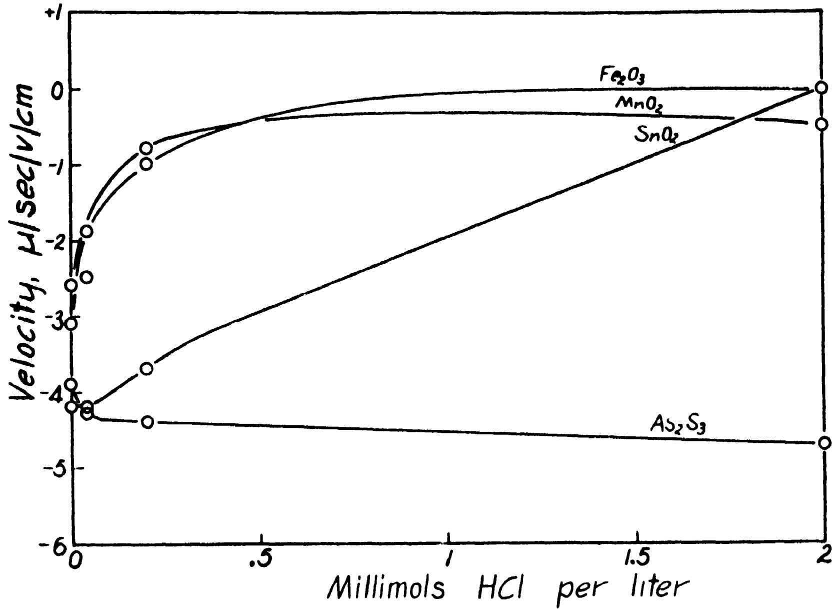

FIG. 9

DISCUSSION

At this point it is necessary to distinguish between lyotropic series associated with the coagulation of sols and the lyotropic series presented here. The former are obtained by determining coagulation values, i.e., by noting the minimum concentration of electrolyte which produces complete precipitation in a given length of time. When different ions are used it is found that different concentrations are required to produce coagulation. The ion which coagulates the sol in the lowest concentration is given first place in the lyotropic series. As a rule the higher the valence of the coagulating ion the more prominent is its position in the series. It has been shown by Powis (4) that coagulation occurs when the stabilizing potential is reduced to 30 millivolts. A critical potential with the above value corresponds to a migration velocity of about 2 μ per second per volt per centimeter in our experiments. Thus we can form an opinion concerning the attributes of an ion as a coagulator from the concentration needed to reduce the mobility of the colloid particles to the critical value.

In the present study the data necessary for deducing lyotropic series were obtained by adding the same concentration of different ions and noting the decrease in mobility of the sol particles. The ion which produced the greatest decrease in velocity was given the leading position in the series, the other ions being placed accordingly

The electrolyte curves in figures 1 to 4 for positive sols are well defined at velocities greater than 2 μ. This fact makes it possible to deduce lyotropic series which would be identical with lyotropic series determined from flocculation values for the same sols.

Figure 7, for manganese dioxide, shows that there is no difference in the concentration of trivalent ions required to reduce the velocity of the particles to the critical value, i.e., to produce coagulation. On entering the unstable zone the curves spread out. This may be interpreted to mean that there is a difference in the degree to which ferric ions, aluminum ions, and chromic ions enter the double layer in the unstable zone. The same phenomenon is shown with negative iron oxide in figure 8. Thus, although flocculation data sometimes fail to indicate the existence of lyotropic effects, they may be present and well defined.

An inspection of the curves in figures 5 to 8 for negative sols shows that the order of coagulating ions can be deduced clearly only in the case of arsenic trisulfide. The lyotropic series is Th > Cr > Al > Fe > Ba > K. In figure 5 the ferric chloride and aluminum chloride curves cross. At a concentration of about 0.15 millimol per liter the two electrolytes are equally effective in decreasing the velocity of the colloid particles. The migration velocity at this concentration is about 0.9 μ per second per volt per centimeter. The low velocity indicates the presence of an excess of electrolyte over that needed for coagulation. At higher concentrations ferric chloride becomes more effective than aluminum chloride in decreasing the velocity. The hydrochloric acid data throw no light on this unexpected behavior. These data do show, however, that the lyotropy with ferric chloride, aluminum chloride, and chromium chloride is not determined by the degree of hydrolysis of the salts. The fact that the curves cross in an unstable region (between -2.0 μ per second per volt per centimeter and the isoelectric point) where the probability of adhesion is high is of doubtful significance. Figure 7 shows that the same phenomenon is encountered in a stable region with recharged manganese dioxide. The electrolyte curves with stannic oxide, plotted in figure 6, are irregular before the first coagulation zone is reached.

Somewhat similar results to these have been obtained by P. Tuorila (6) while investigating the migration velocity of clay suspensions on the addition of electrolytes. For example, at concentrations below 7 millimols per liter silver ion was found to be more effective than potassium ion in reducing the mobility, whereas, at concentrations over 7 millimols per liter potassium ion was more effective than silver ion in this respect. The relation of concentration to the lyotropic series was even more pronounced in the case of sodium permutite suspensions. At concentrations of about 0.0025 *N* the series found by Tuorila is Ba > Sr > Ca > Mg; at about 0.005 *N* the series is Ca > Sr > Ba > Mg; while at 0.015 *N* the series becomes Mg > Ca > Sr > Ba. The same investigator also observed different lyotropic series for different sols, e.g., for a paraffin sol the order of cations is Li > Na > K > Cs > Ag > H, while for a clay suspension the series is Li > Na > Ag, K > Cs > H.

The pure positive sols of this study had markedly different mobilities, e.g., the particles of the chromic oxide sol migrated with a velocity of 4.8 μ per second per volt per centimeter when no added electrolyte was present. The ferric oxide particles had a velocity of 2.7 μ per second per volt per centimeter under the same conditions. A survey of figures 1 to 4 shows that the sulfate ion reduces the velocity of chromic oxide particles to the greatest extent; then follow arsenic trisulfide, iron oxide, and aluminum oxide. Phosphate ion reduces the mobility of the sols in the following order: $Fe_2O_3 > Al_2O_3 > Cr_2O_3 > As_2S_3$. If more were known about the electrical conditions at the interface and if the adsorbabilities of the neutral materials for these ions were known, an explanation for the inversions in order of the sols might be obtained.

B. Effect of Colloids of Opposite Sign on the Stability of Colloidal Systems

The sols used in the mutual coagulation study, as well as the method of measuring migration velocities, were the same as in the sol-electrolyte investigation. In preparing the samples for observation the same method of mixing was followed in each case. That is, the sol which was to be present in the smaller amount was diluted to 50 cc. with distilled water and added to 50 cc. of the pure oppositely-charged sol. The mixture was shaken by hand during the addition and then set aside for one-half hour before making any observations.

The results are shown in figures 10 to 17. In all cases the mixtures had the appearance of homogeneous colloids, i.e., the particles all travel in the same direction with uniform velocity.

DISCUSSION

From an electrokinetic standpoint the behavior of colloids with colloids of opposite sign is strikingly similar to the behavior of colloids with electrolytes that contain a highly adsorbable ion of opposite sign. Thus when either of these substances is added in small amount to a sol, the latter experiences a decrease in mobility and a diminution in stability. When the added substance is a colloid of opposite sign precipitation occurs upon reaching the critical velocity.[3] When an excess of oppositely-charged colloid is mixed with a sol the latter is recharged. In all of these instances the behavior is well-known from electrolyte addition.

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[3] The critical velocity, 2 μ per second per volt per centimeter, observed in these experiments corresponds to a critical potential of 30 millivolts (calculated from the Helmholtz-Perrin formula containing the factor 4)

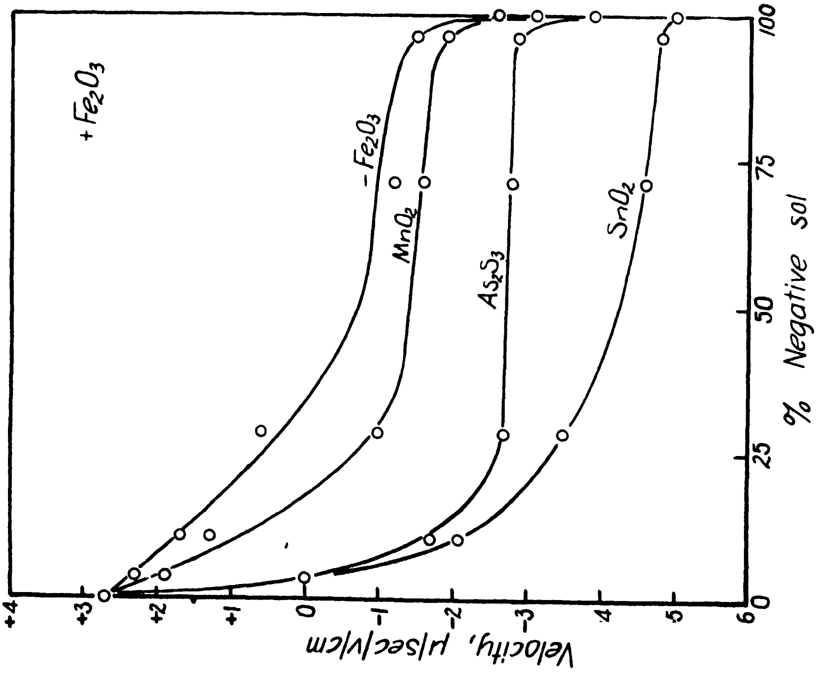
+Fe₂O₃
-Fe₂O₃
MnO₂
As₂S₃
SnO₂
Velocity, μ/sec/v/cm
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
-6
0
25
50
75
100
% Negative sol

FIG. 10

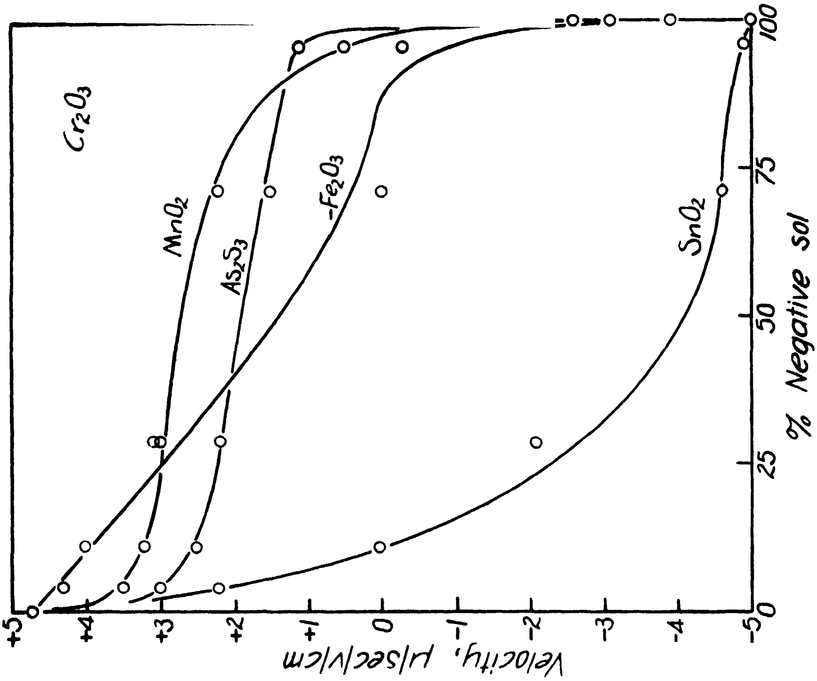
Cr₂O₃
MnO₂
As₂S₃
-Fe₂O₃
SnO₂
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
0
25
50
75
100
% Negative sol

FIG. 11

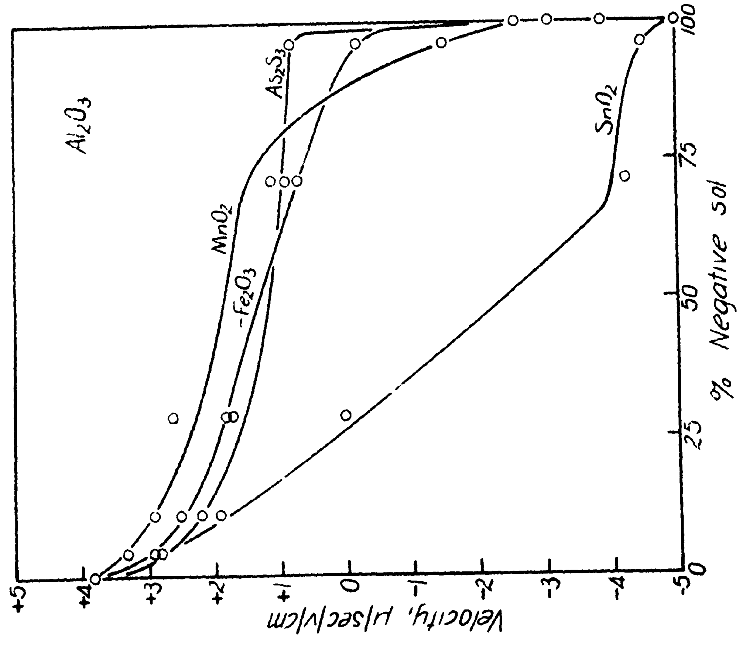
Al_2O_3
MnO_2
$-Fe_2O_3$
As_2S_3
SnO_2
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
0
25
50
75
100
% Negative sol

FIG. 12

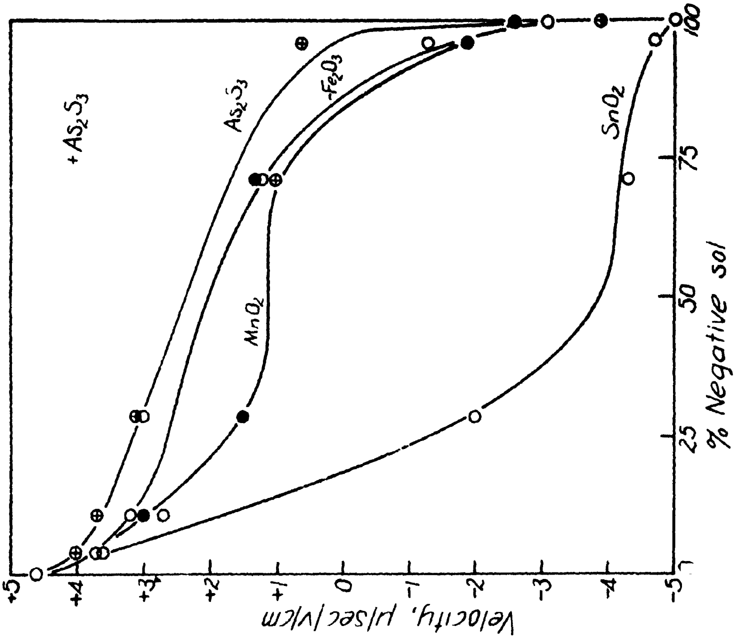
$+As_2S_3$
As_2S_3
$-Fe_2O_3$
MnO_2
SnO_2
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
0
25
50
75
100
% Negative sol

FIG. 13

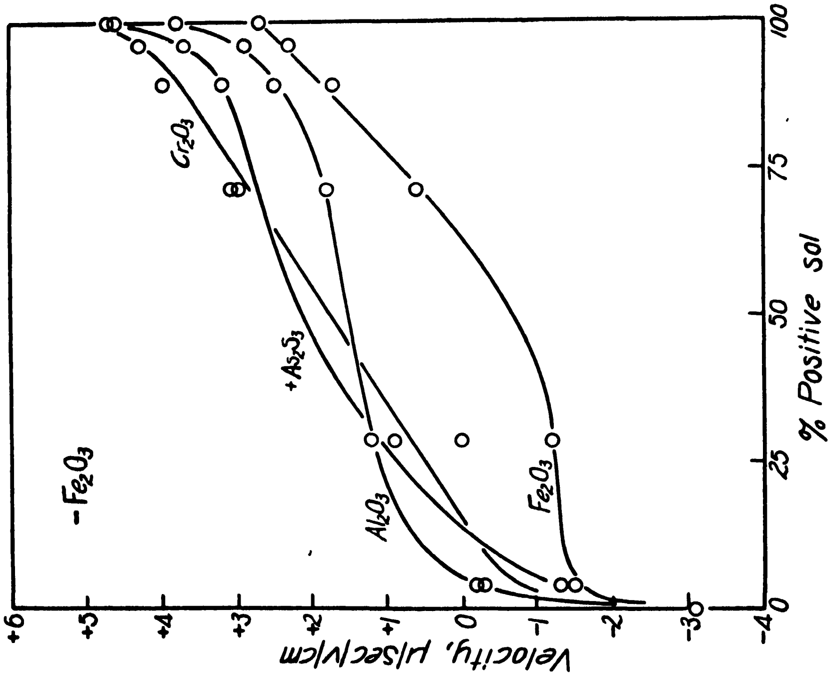
-Fe$_2$O$_3$
Cr$_2$O$_3$
+As$_2$S$_3$
Al$_2$O$_3$
Fe$_2$O$_3$
Velocity, μ/sec/v/cm
+6
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
0
25
50
75
100
% Positive sol

FIG. 14

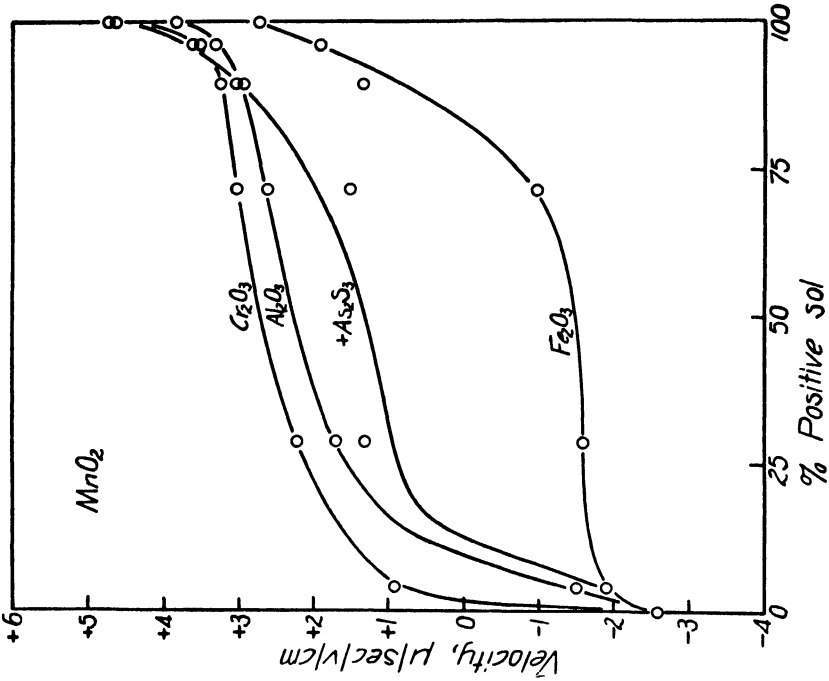
MnO$_2$
Cr$_2$O$_3$
Al$_2$O$_3$
+As$_2$S$_3$
Fe$_2$O$_3$
Velocity, μ/sec/v/cm
+6
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
0
25
50
75
100
% Positive sol

FIG. 15

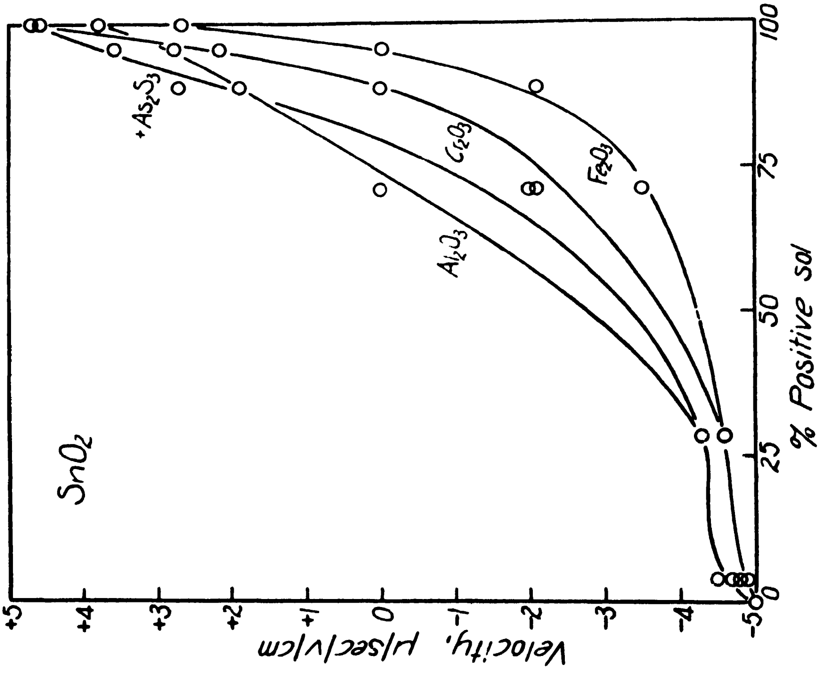
SnO_2
$+As_2S_3$
Cr_2O_3
Fe_2O_3
Al_2O_3
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
Velocity, μ/sec/v/cm
0
25
50
75
100
% Positive sol

FIG. 16

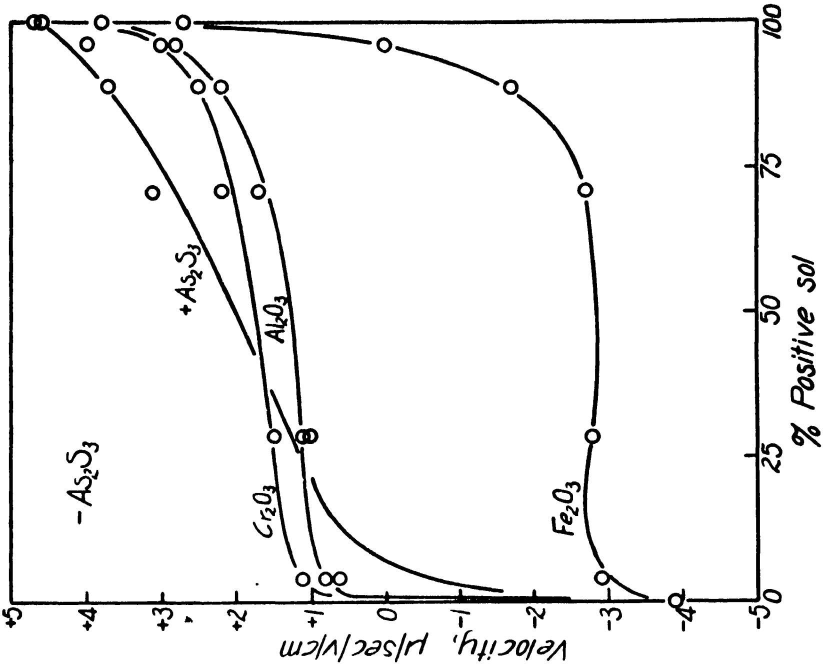
$-As_2S_3$
$+As_2S_3$
Al_2O_3
Cr_2O_3
Fe_2O_3
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
Velocity, μ/sec/v/cm
0
25
50
75
100
% Positive sol

FIG. 17

From an inspection of figures 10 to 17, it is at once apparent that effects analogous to the lyotropy of electrolytes exist. In reporting this lyotropy, however, there is some question as to the method of comparison. Either of two methods may be employed directly with plots between migration velocity and concentration of added substance. That is, any ordinate (concentration = constant) or any abscissa (velocity = constant) might be drawn and the order of the curves cutting these lines would serve as a "lyotropic" series. If flocculation methods are used to study mutual coagulation a third way appears plausible, i.e., assuming the midpoint of the concentration range in the flocculation zone represents the optimum of precipitation and observing the values of these points for the different systems. This method was used by Weiser and Chapman (7). As they observed, the zone of flocculation may be either narrow or broad. The fact that a wide zone exists shows at once that the discharge curve has flattened out, but the position of the curve (from flocculation data) must only be a matter of speculation. Thus the system iron oxide–manganese dioxide (figure 15) would give an optimum, by this method, which really represents a mixture possessing an appreciable negative mobility. Similarly, the systems chromium oxide–arsenic trisulfide, aluminum oxide–arsenic trisulfide (figure 17) give apparent optima which represent mixtures possessing appreciable positive mobilities. Where the coagulation zone is narrow, however, so that the discharge curves pass through as approximately straight lines, then the apparent optimum corresponds with the isoelectric point.

The lyotropy observed in this study may be presented in the following manner.

Velocity = constant = 0

Positive sol	*Order of negative sols*
As_2S_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Fe_2O_3	SnO_2, $As_2S_3 > MnO_2 > Fe_2O_3$
Al_2O_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Cr_2O_3	$SnO_2 > Fe_2O_3 > MnO_2 > As_2S_3$

Negative sol	*Order of positive sols*
As_2S_3	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
Fe_2O_3	$Al_2O_3 > Cr_2O_3 > As_2S_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$

Concentration = constant = 50 per cent

Positive sol	*Order of negative sols*
As_2S_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Fe_2O_3	$SnO_2 > As_2S_3 > MnO_2 > Fe_2O_3$
Al_2O_3	$SnO_2 > Fe_2O_3$, $As_2S_3 > MnO_2$
Cr_2O_3	$SnO_2 > Fe_2O_3 > As_2S_3 > MnO_2$

Negative sol	*Order of positive sols*
As_2S_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
Fe_2O_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$

Since the percentage concentration calculated in all data is a volume percentage and does not refer to the number of particles, the significance of the lyotropy at 50 per cent is doubtful. The point of interest, however, is the fact that it is different from the lyotropy at the isoelectric point.

It will be observed that the lyotropic effects apparent in figures 10 to 13, at low concentration of added sol, are quite different from the lyotropy manifested in the presence of high concentration of added sol. This is analogous to the change in lyotropy with concentration of added electrolyte.

SUMMARY

1. An ultramicroscopic method has been used to follow the changes in stability of sol-electrolyte mixtures and of mixtures of oppositely-charged colloids with changes in concentration.

2. Lyotropic series for the coagulating ions were determined for each colloidal system.

3. In some cases for a given sol the position of ions in the lyotropic series was altered when going from a low concentration to a higher one. Thus the series are, at low and high concentrations, respectively,

For negative arsenic trisulfide	Th > Cr > Al > Fe > Ba > K
	Th > Cr > Fe > Al > Ba > K
For stannic oxide	Th > Al > Cr > Fe > Ba > K
	Al, Th > Ba > Cr > Fe > K
For manganese dioxide	Th > Al > Cr, Fe > Ba > K
	Th > Cr, Fe > Al > Ba > K

4. It has been demonstrated that lyotropic effects, which may be obscure from flocculation data, are shown clearly by cataphoretic measurements.

5. The mobilities of mixtures of oppositely-charged colloids are somewhere between the mobilities of the pure colloids comprising the mixture.

6. The mixtures coagulate when the mobility is lowered to a critical value.

7. Lyotropic series, indicating the relative effectiveness of a number of oppositely-charged sols upon a given sol, have been given.

8. Evidence has been cited to show that the lyotropy encountered varies with the given sols as well as with the concentration of the added colloid.

The authors are indebted to Professors J. H. Walton and C. H. Sorum for their kind interest and helpful suggestions during the course of this study.

REFERENCES

(1) SCHULZE: J. prakt. Chem. **25**, 431 (1882); **27**, 320 (1883).
LINDER AND PICTON: J. Chem. Soc. **67**, 63 (1895); **87**, 1906 (1905).
(2) BANCROFT: J. Phys. Chem. **19**, 363 (1915).
(3) HARDY: J. Physiol. **24**, 288 (1899).
(4) POWIS: Z. physik. Chem. **89**, 186 (1915).
(5) HAZEL AND AYRES: J. Phys. Chem. **35**, 2930 (1931).
(6) TUORILA, P.: Kolloidchem. Beihefte **27**, 44 (1928).
(7) WEISER AND CHAPMAN: J. Phys. Chem. **35**, 543 (1931).

MIGRATION STUDIES WITH COLLOIDS. II

THE MECHANISM OF THE MUTUAL COAGULATION PROCESS

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Received July 20, 1932

INTRODUCTION

The phenomenon to which the term "mutual coagulation" has been applied may be defined as the precipitation occurring when two colloidal systems are mixed. Although noted by Graham (1) in 1862, the first survey of mutual coagulation was made by Linder and Picton (2), who observed that the mutually precipitating sols were of opposite charge. Further, they cited the fact that in mixtures of strongly-negative and weakly-positive sols the resultant migration in an electric field was toward the anode unless a large excess of the positive sol were used. That is, mixtures of oppositely-charged sols are unstable only within certain limits of concentration. These general results were confirmed by a number of investigators (3) but made especially clear by Biltz (4).

In 1910, Lottermoser (5), studying the behavior of mixtures of positive and negative silver iodide sols, attempted to explain the attendant coagulation as a consequence of a reaction between the stabilizing electrolytes—silver nitrate and potassium iodide. Making use of this idea and the well-known fact that certain combinations of negative sols, in which reactions between the peptizing ions might be assumed, are unstable (6), Thomas and Johnston (7) have deduced a general mechanism. Their view that the coagulation in the system ferric oxide–silicic acid is a result of the reaction $H^+ + OH^- = H_2O$ and, as such, should have an optimum where the concentrations of sodium hydroxide and hydrochloric acid are equivalent was upheld over a limited range.

On the other hand Wintgen and Löwenthal (8) were led to conclusions diametrically opposed to a chemical mechanism. In a study of the system chromium oxide–stannic oxide they found that the maximum precipitation corresponds to that calculated from the charge of the particles (determined from transference experiments (9)). The results of Biltz (4) have also been used to show that the electric charge is the dominant factor in mutual coagulation. From his data excerpts have been made to prove the assertion that the order of effectiveness of a series of positive sols does not change if different negative sols are used (10). This practice has not been in vogue since Bancroft (11) pointed out that the importance in Biltz' results lay in the deviations from the order in such series.

Weiser and Chapman (12), considering the widths of the flocculation zones in terms of the concentrations of the mutually precipitating sols, came to the conclusion that the mutual coagulation process may be determined by a number of factors, namely, electrical neutralization, mutual adsorption of the particles, interaction between stabilizing ions, and the presence of excess electrolyte in the sols. They again observed inversions in the precipitating powers of a series of negative sols with a number of positive sols.

It has been demonstrated that the ultramicroscopic technique used with sol-electrolyte systems can be satisfactorily employed in studying the velocities of mixtures of oppositely-charged colloids (13). Since such mixtures appear to behave as homogeneous colloidal systems in the important respect that the particles under the influence of an electric field all migrate in the same direction and with the same velocity, it was believed that some information as to the nature of the units of the systems might be afforded by an investigation of their behavior with electrolytes.

EXPERIMENTAL

In general the systems used in this study were prepared by mixing two of the oppositely-charged colloids used in the previous studies. However, so little of the aluminum oxide and manganese dioxide stock sols remained that these were diluted with an equal volume of water before mixing. Two stock mixtures were made from each pair of oppositely-charged sols—one having a net positive and the other a net negative charge.

The method of adding the electrolyte solutions and observing the migration velocities was the same as that reported for unmixed colloidal systems in the first paper of this series (13), with the exception that the total volume of each sample was 50 cc. rather than 100 cc.

RESULTS

The data for mixtures bearing a net positive charge are plotted in figures 1 to 3. Similar data for mixed sols bearing a net negative charge are plotted in figures 4 to 8.

In all cases it is apparent that the addition of an ion carrying a double charge or greater increases the stability of a mixture possessing a net charge of the same sign. It will also be observed that the phenomenon seems to be different from the usual type of charging of a colloid by a highly adsorbed ion of like charge. Table 1 and the plot of the data therein (figure 9) make this difference more obvious.

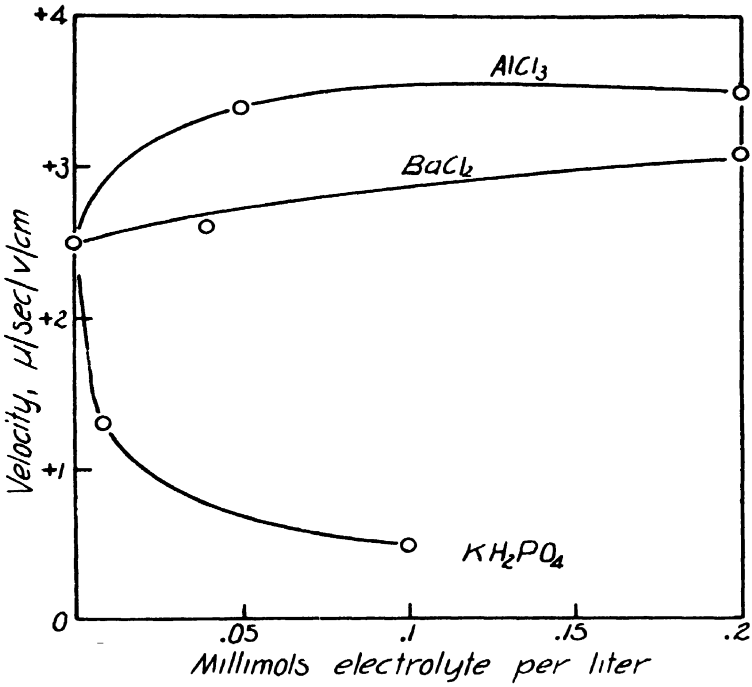

FIG 1. ALUMINUM OXIDE–MANGANESE DIOXIDE MIXTURE
25 cc Al_2O_3; 10 cc MnO_2; 15 cc. H_2O

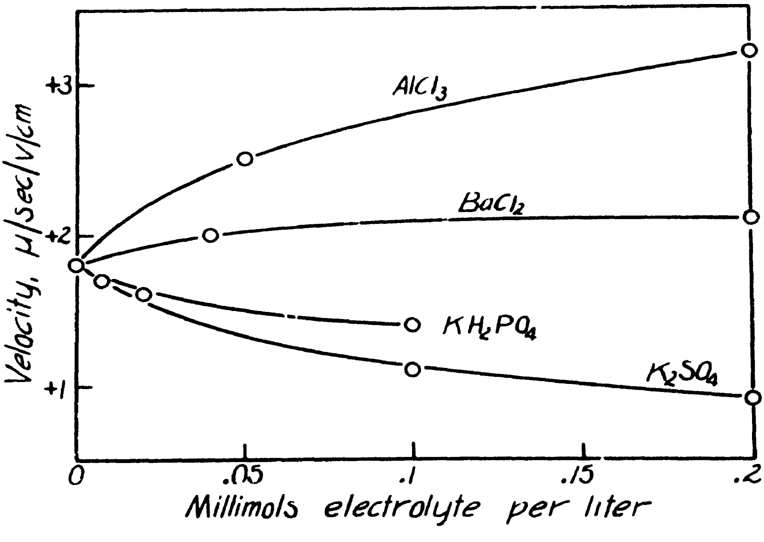

FIG 2. ALUMINUM OXIDE–ARSENIC TRISULFIDE MIXTURE
20 cc. Al_2O_3; 5 cc. As_2S_3; 15 cc. H_2O

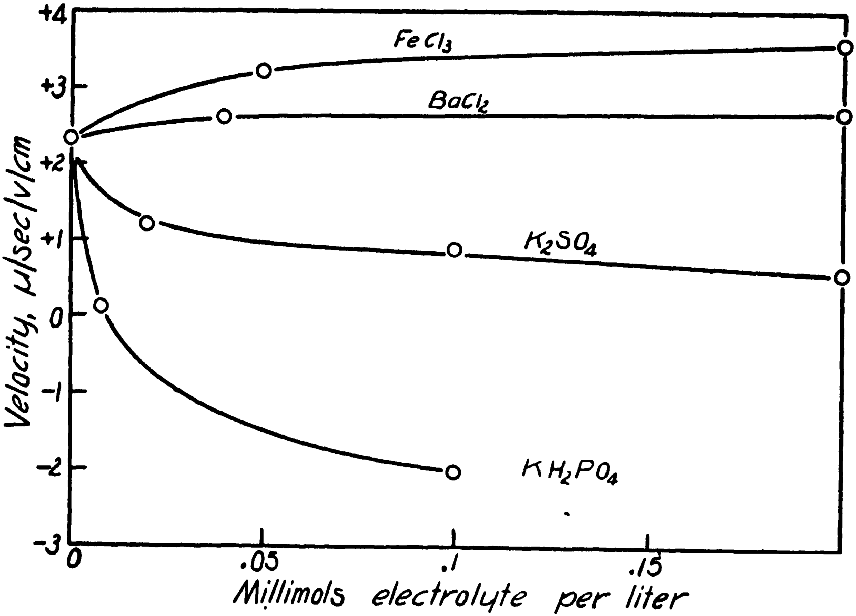

FIG. 3. IRON OXIDE–MANGANESE DIOXIDE MIXTURE
50 cc. Fe_2O_3; 1 cc. MnO_2; 49 cc. H_2O

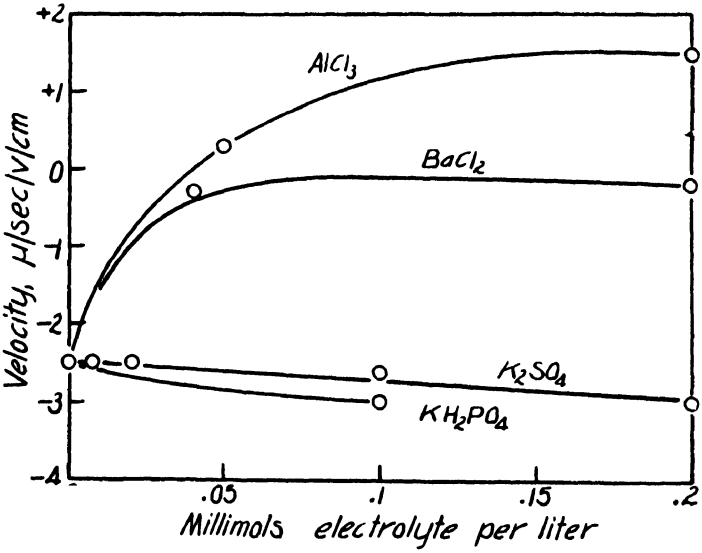

FIG. 4. MANGANESE DIOXIDE–ALUMINUM OXIDE MIXTURE
100 cc. MnO_2; 2 cc. Al_2O_3; 98 cc. H_2O

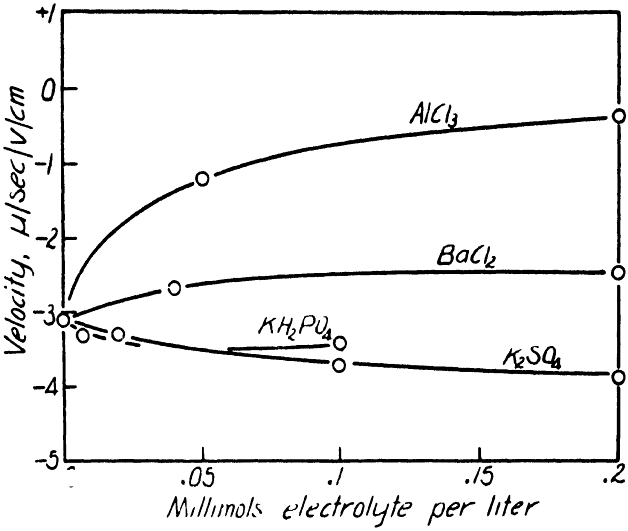

FIG. 5 ARSENIC TRISULFIDE-ALUMINUM OXIDE MIXTURE
50 cc. As_2S_3; 1 cc. Al_2O_3; 49 cc. H_2O

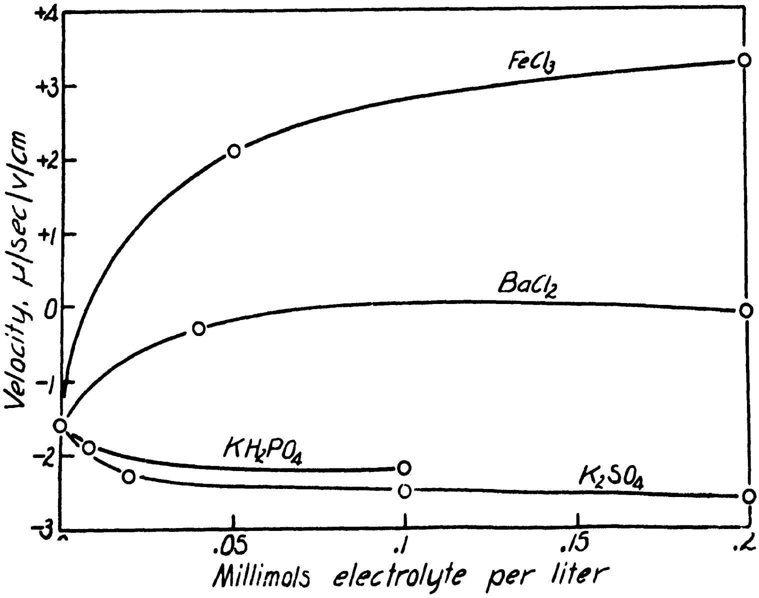

FIG. 6. MANGANESE DIOXIDE-IRON OXIDE MIXTURE
100 cc. MnO_2; 1.5 cc. Fe_2O_3; 98.5 cc. H_2O

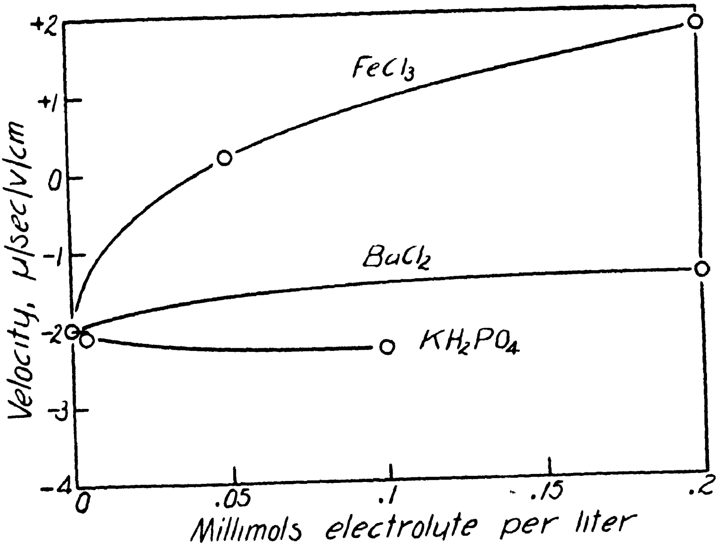

FIG. 7. ARSENIC TRISULFIDE-IRON OXIDE MIXTURE I
25 cc. Fe_2O_3; 10 cc. As_2S_3; 15 cc. H_2O

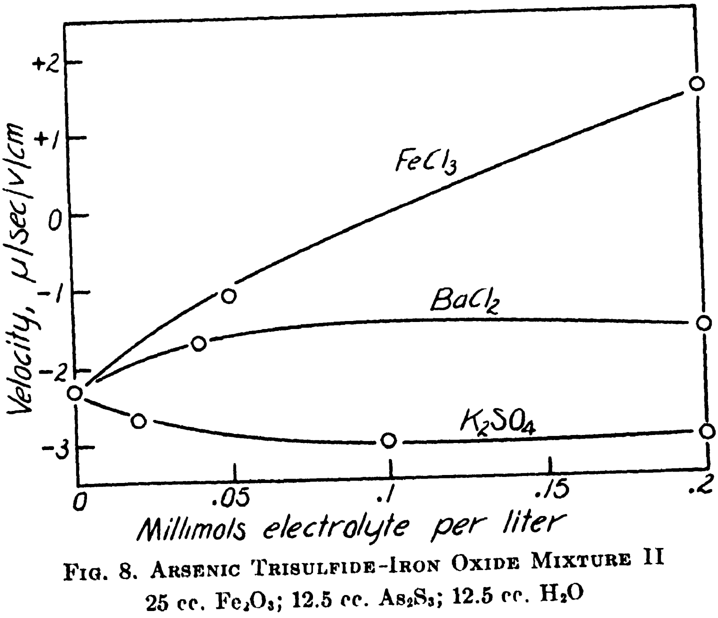

FIG. 8. ARSENIC TRISULFIDE-IRON OXIDE MIXTURE II
25 cc. Fe_2O_3; 12.5 cc. As_2S_3; 12.5 cc. H_2O

TABLE 1

MILLIMOLS $BaCl_2$ PER LITER	TIME IN SECONDS		VELOCITY µ/SEC /V./CM	
	Al_2O_3	Mixture*	Al_2O_3	Mixture*
0	6.7	10.0	+3.6	+2.5
0.2	6.5	7.9	+3.9	+3.1
1.0	7.2	6.8	+3.5	+3.7

* The mixture is the same as that referred to in figure 1, i.e., 25 cc. Al_2O_3, 10 cc. MnO_2, 15 cc. H_2O.

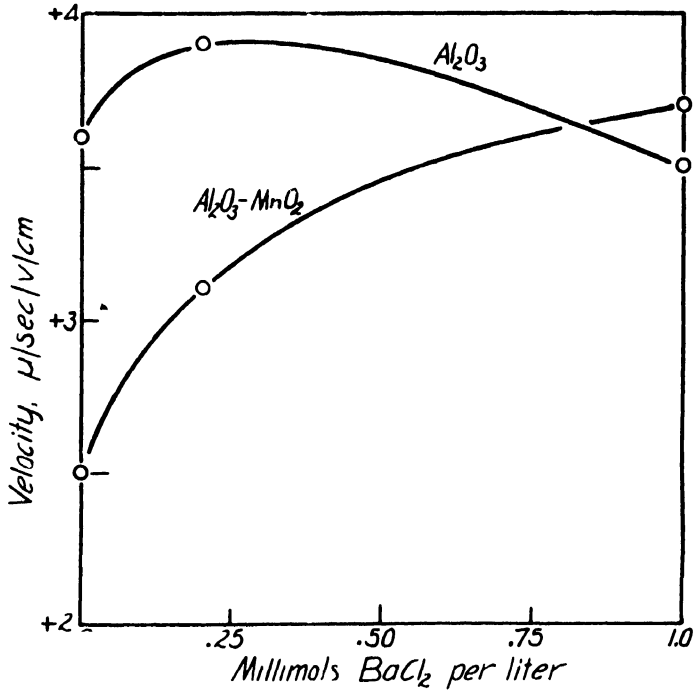

Fig. 9

DISCUSSION

In approaching the subject of mutual coagulation with the purpose of formulating a general theory for its mechanism, we are faced with the fact that in at least two ways a mixture of oppositely-charged colloids behaves like a simple system and in at least one way it is different. The flocculation of a mixed system occurs in the same manner and apparently for the same reasons as that of a "pure" sol. Also, the particles in a mixed system under the influence of an electric field migrate in the same direction and with the same velocity.[1] The deviation from the behavior of a simple, unmixed system is apparent from a consideration of table 1 and figure 9. That is, the charging effect observed when the added ion is of high adsorbability and the same sign does not fall off at moderately high concentrations.

When two oppositely-charged sols are mixed the stability of the system as a whole is lessened in some manner and an agglomeration of particles may or may not take place. Leaving aside for a moment the manner in which the stability is lowered, let us consider the probable nature of the particles in the mixture. If an aggregation does not take place and there are present only single particles of two different chemical substances, one would expect to find two different sets of velocity values in any given system, for the simple reason that in a competition for the excess ions which give the mixture a net positive or negative charge, the adsorbing powers of the substances are not the same.

The environment in which mutual coagulation takes place has been found to be well adapted to a mutual adsorption of the two colloids (14). If adsorption of the oppositely-charged particles does take place, then some clue to the arrangement of the charges around the aggregates might be afforded by the behavior of the mixed system toward electrolytes. An aggregation to compound particles with the excess charges remaining after neutralization distributed uniformly around the aggregates would account for the fact that the particles in a mixed system migrate as single particles, i.e., in the same direction with uniform velocity. Moreover, the effect of electrolytes on the mobility of particles in a mixed system resembles the behavior of systems containing single particles under the same conditions, i.e., the mobility of particles in mixed systems is decreased by addition of ions of opposite sign to the mixture and enhanced by addition of ions of the same sign. However, a simple aggregation with uniform distribution of charges would not account for the fact that the charging effect does not fall off when the antagonistic ion is present in higher concentrations.

From the shape of the curves in figures 1 to 8 it appears as if the increased stabilities of the mixtures were due to a discharge of the colloid of opposite sign present in the system. This may be a consequence of an unequal distribution of charges on the aggregate so that, for example, the arsenic trisulfide particles in a positive aluminum oxide–arsenic trisulfide mixture are still able to adsorb strongly a given cation. The phenomenon appears analogous to the ionic antagonism observed by several investigators (15), but a simple antagonistic effect presumably due to a regular preferential adsorption of an ion by the whole particle would not account for the continued increase in stability at higher electrolyte concentrations. If the adsorption is unequal for the two parts of the double particle, then one would expect the mixtures containing a small amount of one sol to show the charging effect only to a limited degree. That this is borne out is apparent from figures 3 to 6. The concept of an unequal charge distribution making the double particle, in some instances, effectively a distorted dipole with possibly a strong electrostatic attraction holding the component parts together seems to afford the best explanation of the data presented in this paper. An experimental verification or disproof might be furnished by a measurement of the dipole moment of a particle of this type. Under a very high potential gradient it might also be possible, in some cases, to split apart the double particles.

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[1] Although this statement is true for all of the mixed systems reported and also in an overwhelming number of other cases, the authors have encountered systems possessing two different mean velocity values.

The manner in which the stability of the system as a whole is lowered will now be considered. Thomas (16) considers that mutual coagulation is a result of chemical interaction between the ions stabilizing the oppositely-charged sols. As the amount of added sol is increased the stabilizing ion of the added colloid presumably reacts with an equivalent amount of the ion stabilizing the oppositely-charged sol, forming a definite amount of a slightly-ionized compound. Presumably also, there then occurs a redistribution of the excess charges so that the stability of the system is lowered uniformly. At the isoelectric point the two stabilizing ions are in exact chemical equivalence and there are no excess charges. Thus it follows that if one adds the stabilizing ion of a given positive colloid through the medium of an electrolyte, he should reach the isoelectric point of a given negative colloid at the same ionic concentration as in mutual coagulation. The above deduction assumes that all the added ions are effective in causing coagulation. If this is not true, then the ion concentration should be greater in the latter case than in the mutual coagulation process. This premise has been experimentally tested in mixtures of positive and negative ferric oxide sols.

From the migration velocities of positive iron oxide-potassium ferrocyanide mixtures (17) the amount of electrolyte present at the isoelectric point of a given positive sol may be calculated. Then, if a negative ferric oxide sol containing a known amount of potassium ferrocyanide per liter is added to the same positive sol, the electrolyte concentration in the isoelectric mixture may again be determined. A comparison of the two amounts, according to Thomas' theory, should reveal the former to be at least as large as the latter.

The results of the above procedure are given in table 2 for three different positive sols. In this case a mechanism solely dependent on a chemical reaction between the peptizing ions seems improbable. Also, in accounting for the variations in stability of certain mixtures, e.g., arsenic trisulfide–antimony trisulfide (18) and arsenic trisulfide–gamboge (19) on the basis of chemical reactions between the stabilizing ions, one is led to rather implausible speculations.

Various investigators (20) have demonstrated the fact that there exist inversions in orders of effectiveness for a given group of sols with several oppositely-charged sols. On the face of it one would be tempted to conclude that such being the case a unique explanation of mutual coagulation on the basis of electrical neutralization is impossible. That this does not necessarily follow even in the improbable case where no aggregation of particles is assumed, may be readily seen from the following considerations.

If a positive sol composed of n_1 particles, each carrying a charge of q_1 units, be mixed with a negative sol composed of n_2 particles each carrying a charge of q_2 units, the mixed system will contain n_3 particles each bearing a charge of q_3 units and the sign of the mixed colloid will be determined by the relation $n_3q_3 = n_1q_1 + n_2q_2$ (assuming a mere ionic neutralization). In the simplest case $n_3 = n_1 + n_2$. Since the product, n_3q_3, is not measured but is only some function of the charge, q_3, it is necessary to divide through by $n_1 + n_2$. This fact, of itself, may produce inversions in a series for suitable values of n_1q_1 and n_2q_2. When adsorption of the colloid particles takes place, $n_3 \neq n_1 + n_2$ and the inversions will be further complicated.

TABLE 2

Comparison of potassium ferrocyanide concentrations at the isoelectric point

POSITIVE SOL	MILLIMOLS $K_4Fe(CN)_6$ PER LITER	
	Electrolyte	Negative sol
1	0.0008	0.0025
2	0.0022	0.0075
3	0.0033	0.0048

The variations in order of effectiveness of positive sols in decreasing the stability of negative sols observed in the first paper of this series should be scrutinized rigidly with a view of ascertaining whether they are the same as the variations in effectiveness of the stabilizing ions. The stabilizing ions of the positive sols, iron oxide, aluminum oxide, chromium oxide, arsenic trisulfide, may be considered to be H^+ in each case, together with Fe^{+++}, Al^{+++}, and Cr^{+++} for the respective hydrous oxides, and Th^{++++} for arsenic trisulfide. The orders of the above positive sols with negative stannic oxide, manganese dioxide, arsenic trisulfide, and iron oxide have been found (13) to be:

Negative sol	*Order of positive sols*
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
As_2S_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
Fe_2O_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$

whereas the order of the stabilizing ions with the negative sols has been found to be:

Negative sol	*Order of stabilizing ions*
SnO_2	Al, Th > Cr > Fe
MnO_2	Th > Cr, Fe > Al
As_2S_3	Th > Cr > Fe > Al
Fe_2O_3	Th > Cr > Al > Fe

From a comparison of these lyotropic effects it will be seen that there is no direct parallel between the relative effectiveness of the various positive sols and that of their stabilizing ions with the negative sols. Thus, a simple preferential adsorption of the stabilizing ions does not appear to be the effective mechanism in the systems reported in this study.

Boutaric and Perreau (21) in the system positive iron oxide-negative iron oxide have obtained results supporting a simple selective adsorption of the phosphate ion which was stabilizing the negative sol. They found that the amount of phosphate ion per milligram of iron oxide necessary to flocculate the positive sol was the same whether the ion was furnished by an electrolyte or by the negative sol, when the dilution of the system was taken into account. It was believed of interest to perform a similar experiment keeping the amount of ferric oxide the same in each mixture of positive and negative sol and using the ferrocyanide ion (to which iron oxide is more sensitive than to the phosphate ion) as the stabilizing ion of the negative sol. When this was done it was found that the positive sol was isoelectric at a concentration of 0.0022 millimol per liter of potassium ferrocyanide. When the ion was furnished by the negative ferric oxide sol the same amount of ferric oxide was isoelectric at a concentration of 0.0040 millimol per liter. A simple selective adsorption does not explain these results.

The case when a stabilizing ion is in excess need not be considered here since the sols were relatively pure. However, the presence of free electrolyte would obviously render a sol more effective as a precipitating agent and further complicate the mechanism of adsorption.

SUMMARY

1. Data have been presented to show the influence of electrolytes upon the migration velocities of mixtures of positive and negative colloids.

2. The mechanism of the mutual coagulation process has been deduced to be a lowering in stability of the system caused by mutual adsorption of the two colloids with a consequent unequal redistribution of the total charges around the aggregate.

3. A mechanism solely dependent upon chemical reactions between the stabilizing ions or a simple preferential adsorption of one of these ions has been shown to be improbable in the general case.

REFERENCES

(1) Graham: J. Chem. Soc. **15**, 246 (1862).

(2) Linder and Picton: J. Chem. Soc. **71**, 568 (1897).

(3) Lottermoser: Anorganische Kolloide, page 76. Stuttgart (1901).
Neisser and Friedmann: Munch. med. Wochenschr. **51**, 465, 827 (1903–4).
Henri and others: Compt. rend. soc. biol. **55**, 1666 (1903).
Bechhold: Z. physik. Chem. **48**, 385 (1904).

(4) Biltz: Ber. **37**, 1095 (1904).

(5) Lottermoser: Kolloid-Z. **6**, 78 (1910).

(6) Freundlich and Natansohn: Kolloid-Z. **28**, 258 (1920).

(7) Thomas and Johnston: J. Am. Chem. Soc. **45**, 2532 (1923).

(8) Wintgen and Löwenthal: Z. physik. Chem. **109**, 391 (1924).

(9) Freundlich: Kapillarchemie, Vol. II, p. 208. Akademische Verlagsgesellschaft, M. B. H. Leipzig (1932).

(10) Thomas: in Bogue's Colloidal Behavior, Vol. I, pp. 325–6. McGraw-Hill Book Company, New York (1924).

(11) Bancroft: J. Phys. Chem. **19**, 363 (1915).

(12) Weiser and Chapman: J. Phys. Chem. **35**, 543 (1931).

(13) Hazel and McQueen: J. Phys. Chem. **37**, 553 (1933).

(14) Raehlmann: Pfluger's Archiv. ges. Physiol. **112**, 128 (1906).
Bechhold: Z. physik. Chem. **60**, 299 (1907).
Bancroft: Applied Colloid Chemistry, p. 306 et seq. McGraw-Hill Book Company, New York (1926).

(15) Freundlich and Scholz: Kolloidchem. Beihefte **16**, 267 (1922).

(16) Bogue: Colloidal Behavior, Vol. I, p. 329 et seq. McGraw-Hill Book Company, New York (1924).

(17) Hazel and Ayres: J. Phys. Chem. **35**, 2930 (1931).

(18) Jablczynski and Lorentz-Zienkowska: Bull. soc. chim. **37**, 612 (1925).

(19) Boutaric and Dupin: Bull. soc. chim. **43**, 1059 (1928).

(20) Bancroft: J. Phys. Chem. **19**, 363 (1915).
Weiser and Chapman: J. Phys. Chem. **35**, 543 (1931).
Hazel and McQueen: J. Phys. Chem. **37**, 553 (1933).

(21) Boutaric and Perreau: J chim. phys. **27**, 250 (1930).

REFRACTIVITIES OF LIQUID COMPOUNDS OF PHOSPHORUS

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The number of compounds of phosphorus hitherto examined refractometrically is small, the only investigator of an homologous series of such substances being Kowalewski (1). The present work has been undertaken with a view to extension of our knowledge in this field, particularly with respect to types of compounds and their number.

The first to determine the atomic refractivity of phosphorus was Haagen (2), who from measurements on phosphorus trichloride with C light, deduced the value 14.93, in terms of the Gladstone-Dale (3) formula. For the Fraunhofer lines A and H, Gladstone (4) gave the values 18.3 and 21.3, respectively, for the atomic refractivity of fused phosphorus. Zecchini (5) calculated the atomic refractivity of phosphorus in terms both of the Gladstone-Dale and of the Lorenz-Lorentz (6) formulas in eight of its liquid compounds. He found that the value of the Lorenz-Lorentz atomic refractivity of phosphorus for D light was 4.17 in triethyl phosphate and 4.97 in phosphorus oxychloride, whilst for trivalent phosphorus the value varied from 9.47 for triethylphosphine to 9.72 for phosphorus tribromide, including the value 8.10 for ethoxydichlorophosphine. Zecchini's results with solutions of phosphorus compounds are here left out of consideration, and so also his data for triethyl phosphite, on which doubt has been cast by Arbusow and Ivanow (7). Kowalewski, from his measurements on the alkoxydichlorophosphine series, obtained values varying from 7.60 to 8.22. The values derived from the measurements of Arbusow and Ivanow and of Arbusow and Arbusow (8) on the esters of the oxy-acids of phosphorus are given and discussed in the sequel. Johnson (9) has recently measured the refractive indices of three derivatives of methylphenylphosphinic acid for D light; in his paper, without acknowledgment, he uses results experimentally obtained and refractivities calculated by workers in this field, including those due to Kowalewski, Emmett and Jones (10), Grüttner and Wiernik (11), Grüttner and Krause (12), and Jackson, Davies, and Jones (13).

In the present work the refractive indices were measured with Pulfrich refractometers made by Wolz of Bonn and by Zeiss of Jena, with an Abbé refractometer by Hilger of London and a hollow-prism refractometer (14)

TABLE 1

Molecular refractivities of compounds of phosphorus

NO.	SUBSTANCE	TEMPERATURE $t°$	DENSITY $d_{4°}^{t°}$	REFRACTIVE INDEX $n_F^{t°}$	$n_D^{t°}$	$n_C^{t°}$	MOLECULAR REFRACTIVITIES $[R_G]_F$	$[R_G]_D$	$[R_G]_C$	$[R_L]_F$	$[R_L]_D$	$[R_L]_C$	REFERENCES
1	P	44	1 7528	2 1131	—	2 0501	19 70	—	18 58	9 49	—	9 14	D (20)
2		55 3	1 7133	2 0994	—	2 0375	19 90	—	18 78	9 63	—	9 28	D (20)
3	P_2O_3	27 4	1 9317	1 5518	1 5403	1 5358	31 43	30 78	30 52	18 20	17 88	17 76	T. T. (21)
4	PCl_3	14	1 598	1 525	1 516	—	45 13	44 36	—	26 35	25 97	—	M (22)
5		15 4	1 598	1 533	—	1 520	45 82	—	44 70	26 68	—	26 14	N. C. (23)
6		20	1 5774	1 5231	—	1 5083	45 57	—	44 28	26 61	—	25 98	H (2)
7		21	1 5696	1 5235	1 5122	1 5087	45 83	44 84	44 53	26 77	26 28	26 13	J. D. D. (24)
8	$POCl_3$	17	1 68	1 497	1 488	—	45 37	44 55	—	26 72	26 30	—	G. D. (3)
9		25 1	1 666	—	1 460	—	—	42 35	—	—	25 22	—	Z (5)
10		22	1 6619	1 4636	1.4572	1 4544	42 79	42 20	41 94	25 45	25 15	25 02	J. D. D. (24)
11	$PSCl_3$	11 1	1 654	1 575	—	1 563	58 91	—	57 68	33 85	—	33 27	N. C. (23)
12	PBr_3	25	2 88	1 708	1 687	—	66 57	64 59	—	36 66	35 81	—	G. D. (3)
13		26 6	2 859	—	1 697	—	—	66 01	—	—	36 48	—	Z (5)
14		20	2 8761	1 7176	1 6935	1 6864	67 56	65 29	64 62	37 09	36 13	35 84	J. D. D. (24)
15	$P(C_2H_5)_3$	18 6	0 8001	—	1 4580	—	—	67 63	—	—	40 29	—	Z (5)
16	$P(n\text{-}C_3H_7)_3$	25	0 8073	1 4635	1 4560	1 4529	91 97	90 49	89 88	54 70	53 94	53 62	J. D. D. (24)
17	$P(n\text{-}C_4H_9)_3$	25	0 8120	1 4638	1 4570	1 4542	115 52	113 82	113 12	68 70	67 83	67 47	J. D. D. (24)
18	$P(n\text{-}C_5H_{11})_3$	25	0 8206	1 4673	1 4606	1 4578	139 18	137 18	136 35	82 69	81 67	81 24	J. D. D. (24)
19	$P(C_6H_5)(n\text{-}C_3H_7)_2$	25	0 9251	1 5401	1 5283	1 5234	113 36	110 89	109 86	65 86	64 66	64 16	J. D. D. (24)
20	$P(C_6H_5)(n\text{-}C_4H_9)_2$	25	0 9116	1 5326	1 5212	1 5165	129 82	127 04	125 90	75 60	74 24	73 68	J. D. D. (24)
21	$P(C_6H_5)[CH_3 \cdot CH(CH_3) \cdot CH_2]_2$	25	0 9096	1 5289	1 5180	1 5135	129 13	126 47	125 37	75 29	73 98	73 44	J. D. D. (24)
22	$P(C_6H_5)(n\text{-}C_5H_{11})_2$	25	0 9021	1 5251	1 5148	1 5105	145 66	143 81	141 61	85 02	83 62	83 03	J. D. D. (24)
23	$P(C_6H_5)[CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2]_2$	25	0 9061	1 5259	1 5153	1 5109	145 24	142 32	141 10	84 76	83 32	82 72	J. D. D. (24)
24	$P(C_6H_5)[CH_3 \cdot CH(CH_3) \cdot CH_2\ CH_2]_2$	25	0 8996	1 5235	1 5129	1 5085	145 54	142 59	141 37	85 00	83 55	82 98	J. D. D. (24)
25	$P(C_6H_5)(n\text{-}C_6H_{13})_2$	20	0 9006	1 5207	1 5110	1 5067	160 89	157 89	156 56	94 04	92 56	91 90	J. D. D. (24)

26	$P(C_6H_5)(n\text{-}C_7H_{15})_2$	20	0 8946	1 5168	1 5073	1 5033	176 95	173 69	172 32	103 55	101 94	101 26	J. D. D. (24)
27	$P(C_6H_5)(n\text{-}C_8H_{17})_2$	20	0 8899	1 5129	1 5036	1 5000	192 71	189 22	187 86	112 91	111 18	110 51	J. D. D. (24)
28	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_3H_7)_2$	25	0 9210	1 5390	1 5272	1 5224	121 84	119 17	118 08	70 81	69 52	68 99	J. D. D. (24)
29	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_4H_9)_2$	25	0 9077	1 5325	1 5214	1 5168	138 58	135 69	134 49	80 70	79 29	78 70	J. D. D. (24)
30	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_5H_{11})_2$	25	0 8981	1 5249	1 5144	1 5101	154 44	151 35	150 09	90 16	88 64	88 01	J. D. D. (24)
31	$P(p\text{-}CH_3\cdot C_6H_4)[CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_3]_2$	25	0 9022	1 5249	1 5145	1 5102	153 76	150 71	149 45	89 75	88 26	87 64	J. D. D. (24)
32	$P(p\text{-}CH_3\cdot C_6H_4)[CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH_3]_2$	25	0 8941	1 5232	1 5127	1 5084	154 63	151 53	150 26	90 31	88 79	88 16	J. D. D. (24)
33	$P(p\text{-}CH_3\cdot C_6H_4)[CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH_3]_2$	25	0 8882	1 5137	1 5041	1 5001	169 06	165 90	164 59	99 03	97 46	96 81	J. D. D. (24)
34	$P(p\text{-}CH_3\cdot CH_2C_6H_4)(n\text{-}C_3H_7)_2$	25	0 9147	1 5370	1 5255	1 5208	130 45	127 65	126 51	75 87	74 51	73 95	J. D. D. (24)
35	$P(p\text{-}CH_3\cdot CH_2C_6H_4)(n\text{-}C_4H_9)_2$	25	0 9042	1 5319	1 5208	1 5162	147 20	144 13	142 86	85 75	84 24	83 62	J. D. D. (24)
36	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(C_2H_5)_2$	25	0 9393	1 5533	1 5405	1 5355	114 42	111 77	110 74	66 21	64 94	64 43	J. D. D. (24)
37	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(n\text{-}C_3H_7)_2$	25	0 9282	1 5430	1 5313	1 5266	130 04	127 24	126 11	75 49	74 13	73 58	J. D. D. (24)
38	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(n\text{-}C_4H_9)_2$	25	0 9125	1 5335	1 5229	1 5182	146 36	143 45	142 16	85 21	83 79	83 16	J. D. D. (24)
39	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)_2$	25	0 9738	1 5477	1 5352	1 5301	126 09	123 21	122 04	73 09	71 70	71 13	J. D. D. (24)
40	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_4H_9)_2$	25	0 9600	1 5389	1 5274	1 5226	141 58	138 56	137 30	82 29	80 82	80 21	J. D. D. (24)
41	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_5H_{11})_2$	25	0 9382	1 5289	1 5178	1 5132	157 99	154 67	153 30	92 11	90 49	89 81	J. D. D. (24)
42	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(CH_3)_2$	20	1 1037	1 6243	1 6074	1 6005	130 18	126 65	125 21	73 65	72 05	71 38	J. D. D. (24)
43	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(C_2H_5)_2$	20	1 0711	1 6079	1 5918	—	146 52	142 64	—	83 34	81 54	—	J D D (24)
44	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)_2$	20	1 0562	1 5993	1 5838	1 5774	162 40	158 19	156 46	92 61	90 66	89 85	J. D D. (24)
45	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(n\text{-}C_4H_9)_2$	20	1 0310	1 5847	1 5705	1 5647	178 21	173 88	172 11	102 10	100 07	99 23	J. D. D. (24)
46	$(CH_2)_4{>}P\cdot C_6H_5$	22 5	1 0335	—	1 5894	—	—	93 60	—	—	53 55	—	G. K. (12)
47	$(CH_2)_5{>}P\cdot C_6H_5$	20	1 0317	—	1 5886	—	—	101 63	—	—	58 16	—	G. W. (11)
48	$(CH_2)_5{>}P\cdot C_6H_4\cdot CH_3\text{-}p$	22 2	0 9991	—	1 5729	—	—	110 14	—	—	63 37	—	G. W. (11)
49	$C_6H_5PCl_2$	5 8	1 3369	—	1 6050	1 5984	—	80 99	80 11	—	46 61	45 70	Z (5)
50		7	1 3351	—	1 6053	1 5987	—	81 15	80 26	—	46 19	45 78	Z (5)
51	$(p\text{-}CH_3\cdot CH_2\cdot C_6H_4)PCl_2$	25	1 2250	1 5930	1 5775	1 5711	100 21	97 59	96 51	57 26	56 04	55 53	J. D. D. (24)
52	$[2,5\text{-}(CH_3)_2C_6H_3]PCl_2$	25	1 2371	1 6016	1 5857	1 5791	100 66	98 00	96 90	57 37	56 14	55 62	J. D. D. (24)
53	$(p\text{-}CH_3O\cdot C_6H_4)PCl_2$	25	1 3303	1 6184	1 6000	1 5924	97 15	94 26	93 07	55 07	53 75	53 19	J. D. D. (24)
54	CH_3OPCl_2	20	1 3980	—	1 4773	—	—	45 39	—	—	26 89	—	K (1)
55	$C_2H_5OPCl_2$	20	1 2857	—	1 4718	—	—	53 93	—	—	32 00	—	K (1)
56		24 5	1 2718	—	1 4641	1 4609	—	53 63	53 26	—	31 90	31 70	Z (5)
57	$n\text{-}C_3H_7OPCl_2$	20	1 2278	—	1 4660	—	—	61 11	—	—	36 32	—	K (1)

TABLE 1—*Concluded*

NO	SUBSTANCE	TEMPERATURE t°	DENSITY $d^{t^\circ}_{4^\circ}$	REFRACTIVE INDEX			MOLECULAR REFRACTIVITIES						REFERENCES
				$n^{t^\circ}_F$	$n^{t^\circ}_D$	$n^{t^\circ}_C$	$[R_G]F$	$[R_G]D$	$[R_G]C$	$[R_L]F$	$[R_L]D$	$[R_L]C$	
58	n-$C_4H_9OPCl_2$	20	1 1657	—	1 4608	—	—	69 19	—	—	41 18	—	K (1)
59	$(C_2H_5\cdot O)_2PCl$	20	1 0746	—	1 4350	—	—	63 38	—	—	38 02	—	A. A. (8)
60	$OPH(OC_2H_5)_2$	20	1 0757	1 4130	1 4082	1 4062	53 03	52 41	52 16	32 02	31 69	31 55	A. I. (7)
61		20	1 0734	—	1 4082	—	—	52 52	—	—	31 76	—	A. A. (8)
62		20	1 0720	1 4151	1 4101	1 4081	53 48	52 83	52 58	32 27	31 93	31 79	J. D. D. (24)
63	$P(OC_2H_5)_3$	20	0 9687	1 4192	1 4131	1 4107	71 89	70 85	70 45	43 33	42 78	42 56	A. I. (7)
64		20	0 9574	—	1 4132	—	—	71 70	—	—	43 29	—	A. A. (8)
65		20	0 9629	1 4186	1 4127	1 4098	72 23	71 21	70 71	43 54	43 00	42 73	J. D. D. (24)
66	$[CH_3\cdot CH(CH_3)\cdot CH_2O]_3P$	25	0 8969	1 4283	1 4225	1 4201	119 49	117 88	117 21	71 80	70 97	70 62	J. D. D. (24)
67	$(n\text{-}C_5H_{11}\cdot O)_3P$	25	0 9023	1 4412	1 4353	1 4329	142 92	141 01	140 23	85 57	84 57	84 17	J. D. D. (24)
68	$OP(C_2H_5)(OC_2H_5)_2$	20	1 0259	1 4211	1 4163	1 4143	68 20	67 42	67 11	41 07	40 66	40 50	A. I. (7)
69	$(C_2H_5\cdot O)_4P_2O_2$	20	1 1268	—	1 4284	—	—	104 25	—	—	62 66	—	A. A. (8)
70	$(C_2H_5\cdot O)_4P_2O_3$	20	1 1846	—	1 4222	—	—	103 43	—	—	62 28	—	A. A. (8)
71	$(C_2H_5\cdot O)_4P_2O_2S$	20	1 1885	—	1 4508	—	—	116 16	—	—	69 35	—	A. A. (8)
72	$(C_2H_5\cdot O)_2PO\cdot O\cdot PO(O\ C_2H_5)(C_2H_5)$	20	1 1526	—	1 4280	—	—	101 82	—	—	61 21	—	A. A. (8)
73	$(CH_3\cdot O)_3PO$	25	1 2052	1 3990	1 3950	1 3934	46 38	45 91	45 73	28 12	27 87	27 77	J. D. D. (24)
74	$(C_2H_5\cdot O)_3PO$	5 7	1 0822	—	1 4107	—	—	69 11	—	—	41 76	—	Z (5)
75		17 1	1 0701	—	1 4067	—	—	69 23	—	—	41 89	—	Z (5)
76		20	1 0682	1 4107	1 4062	1 4044	70 04	69 26	68 95	42 31	41 90	41 73	A. I. (7)
77		28 1	1 0618	—	1 4027	—	—	69 07	—	—	41 83	—	Z (5)
78		25	1 0637	1 4082	1 4039	1 4021	69 90	69 16	68 85	42 26	41 87	41 70	J. D. D. (24)
79	$(n\text{-}C_3H_7\cdot O)_3PO$	25	1 0023	1 4182	1 4136	1 4118	93 54	92 51	92 11	56 39	55 85	55 63	J. D. D. (24)
80	$(n\text{-}C_4H_9\cdot O)_3PO$	25	0 9727	1 4274	1 4224	1 4203	116 99	115 62	115 05	70 33	69 61	69 31	J. D. D. (24)
81	$[CH_3\cdot CH(CH_3)\cdot CH_2\cdot O]_3PO$	25	0 9617	1 4222	1 4173	1 4152	116 89	115 53	114 95	70 38	69 66	69 36	J. D. D. (24)
82	$(n\text{-}C_5H_{11}\cdot O)_3PO$	25	0 9497	1 4332	1 4283	1 4262	140 62	139 03	138 35	84 40	83 56	83 21	J. D. D. (24)
83	$SP(OCH_3)_3$	10 5	1 2112	—	1 4583	1 4552	—	59 08	58 69	—	35 20	34 99	E. J. (10)
84	$CH_3SPO(OCH_3)_2$	10	1 2565	—	1 4683	1 4660	—	58 24	57 91	—	34 59	34.42	E. J. (10)

by Bellingham and Stanley of London. The last named instrument was used for acid halides. These refractometers were frequently standardized by the use of water and of benzene. Where refractive indices were measured at temperatures other than the standard temperature of the instrument, the necessary corrections were applied. To ensure constancy of temperature a stream of water, electrically warmed by means of a Bowden (15) pre-heater, was passed through the Pulfrich and Abbé refractometers during the measurements.

The compounds of phosphorus used in this investigation were prepared by methods (16) already described and were redistilled under low pressure immediately before the measurements of density and of refractive index were made. In every case the constant-boiling, middle fraction was chosen. Temperatures were corrected for thermometric errors and densities for air-buoyancy. In view of the ease of oxidation of many of these compounds, due precautions were observed to prevent protracted contact with air.

In table 1 are given densities, d; refractive indices, n, for the F, D, and C lines; molecular refractivities, $[R_G]$, calculated by means of the Gladstone-Dale expression, $(n-1)M/d$; molecular refractivities, $[R_L]$, calculated with the Lorenz-Lorentz formula, $(n^2-1)M/(n^2+2)d$; and references. The molecular weights M, have been calculated on the basis of the international atomic weights (17) for 1932. From this table are excluded all refractive indices for the G′ hydrogen line, for the green lithium line, and for the red cadmium line, the refractive index of phosphine determined by Bleekrode (18), which has been criticized by Brühl (19), that of triethyl phosphite by Zecchini (5), whose preparation had suffered oxidation, and that of isoamyloxydichlorophosphine measured by Kowalewski (1).

Table 2 contains the values of the atomic refractivity of phosphorus and of the group refractivities of certain of its radicals in terms of both the Gladstone-Dale and the Lorenz-Lorentz expressions.

The refractivities given in table 2 have been found by deducting Eisenlohr's (24) values of the refractivities of carbon, hydrogen, ether oxygen, chlorine, and bromine from the Lorenz-Lorentz molecular refractivities given in table 1. That for ether oxygen has been used only when oxygen is present in the group $\equiv$C—O—C$\equiv$. The Gladstone-Dale values employed are given in table 3.

Analysis of tables 1 and 2 reveals the following facts.

(a) In the case of the trialkylphosphines, deduction of Eisenlohr's refractivities of carbon and hydrogen for D light from the molecular refractivities leaves a constant remainder of mean value, 9.14; this would seem to indicate that Eisenlohr's values for carbon and hydrogen hold in the case of these phosphines, and that in them the atomic refractivity of phosphorus for D light is 9.14. The corresponding Gladstone-Dale constant is 14.23.

TABLE 2

Atomic and group refractivities

NO.	SUBSTANCE	ATOM OR GROUP	GLADSTONE-DALE F	GLADSTONE-DALE D	GLADSTONE-DALE C	LORENZ-LORENTZ F	LORENZ-LORENTZ D	LORENZ-LORENTZ C
1	P	P	19 70	—	18 58	9 49	—	9 14
2		P	19 90	—	18 78	9 63	—	9 28
3	P_2O_3	P_2O_3	31 43	30 78	30 52	18 20	17 88	17 76
4	PCl_3	P	13 84	13 46	—	8 22	8 07	—
5		P	14 53	—	13 98	8 55	—	8 34
6		P	14 28	—	13 56	8 48	—	8 18
7		P	14 54	13 94	13 81	8 64	8 38	8 33
8	$POCl_3$	PO	14 08	13 65	—	8 59	8 40	—
9		PO	—	11 45	—	—	7 32	—
10		PO	11 50	11 30	11 22	7 32	7 25	7 22
11	$PSCl_3$	PS	27 62	—	26 96	15 72	—	15 47
12	PBr_3	P	17 85	16 59	—	9 66	9 21	—
13		P	—	18 01	—	—	9 88	—
14		P	18 84	17 29	16 95	10 09	9 53	9 43
15	$P(C_2H_5)_3$	P	—	14 91	—	—	9 28	—
16	$P(n\text{-}C_3H_7)_3$	P	14 87	14 22	13 96	9 34	9 08	8 97
17	$P(n\text{-}C_4H_9)_3$	P	14 61	14 00	13 76	9 34	9 11	9 03
18	$P(n\text{-}C_5H_{11})_3$	P	14 47	13 80	13 54	9 32	9 10	9 01
19	$P(C_6H_5)(n\text{-}C_3H_7)_2$	P	18 24	17 11	16 69	9 95	9 54	9 40
20	$P(C_6H_5)(n\text{-}C_4H_9)_2$	P	18 83	17 56	17 10	10 35	9 89	9 72
21	$P(C_6H_5)[CH_3 \cdot CH(CH_3) \cdot CH_2]_2$	P	18 14	16 99	16 57	10 04	9 63	9 48
22	$P(C_6H_5)(n\text{-}C_5H_{11})_2$	P	18 80	18 63	17 18	10 43	10 03	9 88
23	$P(C_6H_5)[CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2]_2$	P	18 38	17 14	16 67	10 17	9 73	9 57
24	$P(C_6H_5)[CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2]_2$	P	18 68	17 41	16 94	10 41	9 96	9 83
25	$P(C_6H_5)(n\text{-}C_6H_{13})_2$	P	18 16	17 01	16 49	10 12	9 74	9 56
26	$P(C_6H_5)(n\text{-}C_7H_{15})_2$	P	18 35	17 11	16 62	10 29	9 88	9 72

27	$P(C_6H_5)(n\text{-}C_8H_{17})_2$	P	18.24	16.93	16.53	10.32	9.88	9.78
28	$P(p\text{-}CH_3\ C_6H_4)(n\text{-}C_3H_7)_2$	P	18.78	17.54	17.09	10.23	9.79	9.63
29	$P(p\text{-}CH_3\ C_6H_4)(n\text{-}C_4H_9)_2$	P	19.65	18.36	17.87	10.78	10.32	10.15
30	$P(p\text{-}CH_3\ C_6H_4)(n\text{-}C_5H_{11})_2$	P	19.65	18.33	17.84	10.91	10.43	10.26
31	$P(p\text{-}CH_3\ C_6H_4)[CH_3\ CH_2\ CH(CH_3)\ CH_2]_2$	P	18.96	17.68	17.20	10.50	10.05	9.89
32	$P(p\text{-}CH_3\ C_6H_4)[CH_3\ CH(CH_3)\ CH_2\ CH_2]_2$	P	19.84	18.50	18.01	11.06	10.58	10.41
33	$P(p\text{-}CH_3\ C_6H_4)[CH_3\ CH(CH_3)\ CH_2\ CH_2\ CH_2]$	P	18.39	17.17	16.70	10.44	10.02	9.87
34	$P(p\text{-}CH_3\ CH_2C_6H_4)(n\text{-}C_3H_7)_2$	P	19.46	18.17	17.70	10.62	10.16	9.99
35	$P(p\text{-}CH_3\ CH_2C_6H_4)(n\text{-}C_4H_9)$	P	20.34	18.95	18.42	11.16	10.65	10.47
36	$[2,5\text{-}(CH_3)_2C_6H_3]\ P(C_2H_5)_2$	P	19.30	18.00	17.56	10.30	9.82	9.67
37	$2,5\text{-}(CH_3)_2C_6H_3]\ P(n\text{-}C_3H_7)$	P	19.05	17.76	17.30	10.24	9.78	9.62
38	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(n\text{-}C_4H_9)_2$	P	19.50	18.27	17.72	10.62	10.20	10.01
39	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)$	P	20.18	18.74	18.21	10.86	10.32	10.13
40	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_4H_9)_2$	P	19.80	18.39	17.84	10.72	10.21	10.02
41	$(p\text{-}CH_3O\cdot C_6H_4)\ P(n\text{-}C_5H_{11})$	P	20.34	18.80	18.21	11.21	10.64	10.42
42	$(p\text{-}C_6H_5O\cdot C_6H_4)\ P(CH_3)_2$	P	22.11	20.38	19.75	10.20	9.66	9.46
43	$(p\text{-}C_6H_5O\ C_6H_4)\cdot P(C_2H_5)_2$	P	22.58	20.67	–	10.55	9.91	—
44	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)_2$	P	22.59	20.51	19.74	10.49	9.79	9.54
45	$(p\text{-}C_6H_5O\cdot C_6H_4)\ P(n\text{-}C_4H_9)_2$	P	22.53	20.50	19.76	10.64	9.97	9.73
46	$(CH_2)_4{>}P\cdot C_6H_5$	P	—	19.27	—	—	9.87	—
47	$(CH_2)_5{>}P\cdot C_6H_5$	P	–	19.45	—	—	9.86	—
48	$(CH_2)_5{>}P\cdot C_6H_4\cdot CH_3\text{-}p$	P	—	20.11	—	-	10.45	—
49	$C_6H_5PCl_2$	P	–	17.46	17.07	—	9.47	8.84
50		P	—	17.62	17.22	—	9.05	8.92
51	$(p\text{-}CH_3\cdot CH_2\cdot C_6H_4)PCl_2$	P	19.76	18.36	17.83	10.16	9.66	9.47
52	$[2,5\text{-}(CH_3)_2C_6H_3]PCl_2$	P	20.21	18.77	18.22	10.27	9.76	9.56
53	$(p\text{-}CH_3O\cdot C_6H_4)PCl_2$	P	21.78	20.04	19.37	10.99	10.35	10.09
54	CH_3OPCl_2	PO	—	15.07	—	—	9.24	—
55	$C_2H_5OPCl_2$	PO	—	15.76	—	—	9.73	—
56		PO	—	15.46	15.29	—	9.63	9.55
57	$n\text{-}C_3H_7OPCl_2$	PO	—	15.09	—	—	9.43	—

TABLE 2—*Concluded*

NO	SUBSTANCE	ATOM OR GROUP	GLADSTONE-DALE			LORENZ-LORENTZ		
			F	D	C	F	D	C
58	n-$C_4H_9OPCl_2$	PO	—	15 32	—	—	9 67	—
59	$(C_2H_5\cdot O)_2PCl$	PO_2	—	28 24	—	—	11 38	—
60	$OPH(OC_2H_5)_2$	PO_3	15 60	15 40	15 32	10 00	9 92	9 89
61		PO_3	—	15 51	—	—	9 99	—
62		PO_3	16 05	15 82	15 74	10 25	10 16	10 13
63	$P(OC_2H_5)_3$	PO_3	18 59	18 13	17 98	11 98	11 77	11 70
64		PO_3	—	18 98	—	—	12 28	—
65		PO_3	18 93	18 49	18 24	12 19	11 99	11 87
66	$[CH_3\cdot CH(CH_3)\cdot CH_2\cdot O]_3P$	PO_3	18 58	18 06	17 85	12 44	12 25	12 18
67	$(n$-$C_5H_{11}\cdot O)_3P$	PO_3	17 81	17 63	17 42	12 20	12 00	11 94
68	$OP(C_2H_5)(OC_2H_5)_2$	PO_3	14 90	14 70	14 64	9 72	9 65	9 64
69	$(C_2H_5\cdot O)_4P_2O_2$	P_2O_6	—	33 96	—	—	21 32	—
70	$(C_2H_5\cdot O)_4P_2O_3$	P_2O_7	—	33 14	—	—	20 94	—
71	$(C_2H_5\cdot O)_4P_2O_2S$	P_2O_6S	—	45 87	—	—	28 01	—
72	$(C_2H_5\cdot O)_2PO\cdot O\cdot PO(O\cdot C_2H_5)(C_2H_5)$	P_2O_6	—	31 53	—	—	19 87	—
73	$(CH_3\cdot O)_3PO$	PO_4	16 89	16 75	16 71	10 77	10 72	10 70
74	$(C_2H_5\cdot O)_3PO$	PO_4	—	16 39	—	—	10 75	—
75		PO_4	—	16 51	—	—	10 88	—
76		PO_4	16 74	16 54	16 48	10 96	10 89	10 87
77		PO_4	—	16 35	—	—	10 82	—
78		PO_4	16 60	16 36	16 38	10 91	10 86	10 84
79	$(n$-$C_3H_7\cdot O)_3PO$	PO_4	16 44	16 24	16 19	11 03	10 99	10 98
80	$(n$-$C_4H_9\cdot O)_3PO$	PO_4	16 08	15 80	15 69	10 97	10 89	10 87
81	$[CH_3\cdot CH(CH_3)\cdot CH_2\cdot O]_3PO$	PO_4	15 98	15 71	15 59	11 02	10 94	10 92
82	$(n$-$C_5H_{11}\cdot O)_3PO$	PO_4	15 91	15 65	15 54	11 04	10 99	10 98
83	$SP(OCH_3)_3$	PO_3S	—	29 92	29 67	—	18 05	17 92
84	$CH_3SPO(OCH_3)_2$	PO_3S	—	29 08	28 89	—	17 44	17 35

(b) It will also be seen that the former value also holds good for liquid phosphorus itself. The discrepancy between the Gladstone-Dale values is to be attributed to the exceptionally high refractive index of fused phosphorus.

(c) The atomic refractivity of phosphorus in phosphorus trichloride is distinctly different from that in phosphorus tribromide or from that in trialkylphosphines. This shows that when the linkage of phosphorus to carbon is taken as standard, the linkages of phosphorus to halogens possess specific effects. Alternatively, it might be considered that when linked to phosphorus, chlorine and bromine do not possess the same atomic refractivities as when they are linked to carbon, and, consequently, that Eisenlohr's values for the halogens are inapplicable here.

(d) The attachment of an aryl group to a phosphorus atom is a cause of optical exaltation, an indication of the presence of loosely held electrons of low frequency of oscillation, and, consequently, of the appearance of absorption bands at abnormally long wave-lengths. The similar exaltative effect of aromatic groups attached to nitrogen has been attributed to the establishment of a virtual conjugation involving the nitrogen atom and the endocyclic double bonds (28).

TABLE 3

Gladstone-Dale atomic and bond refractivities

ATOM OR BOND	REFRACTIVITY		
	F	D	C
Carbon	4 145	4 111	4 102
Hydrogen	1 895	1 870	1 857
Ether oxygen	2 856	2 845	2 839
Chlorine	10 43	10 30	10 24
Bromine .	16 24	16 00	15 89
Ethylene bond	3 126	2 970	2 889

(e) The interposition of an oxygen atom between an atom of carbon and one of phosphorus raises the molecular refractivity by an amount different from that due to ether oxygen. In fact, the atomic refractivity of oxygen in the $\equiv C{-}O\ P=$ group may be evaluated in the following ways:

(1) Subtraction of the molecular refractivity of

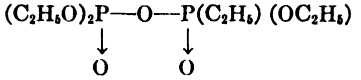
$$O \leftarrow P(C_2H_5)(OC_2H_5)_2 \text{ (No. 68, table 1)}$$

from that of

$$O \leftarrow P(OC_2H_5)_3 \text{ (No. 74)}$$

which gives 1.10 for D light.

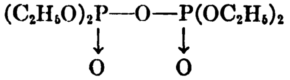
(2) Subtraction of the molecular refractivity of



$$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}(C_2H_5)\,(OC_2H_5)$$

(No. 72)

from that of



$$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}(OC_2H_5)_2$$

(No. 70)

which gives 1.07.

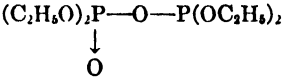
(3) Subtraction of the atomic refractivity of phosphorus, 9.14, from the mean value of the group refractivity for PO_3 in the trialkyl phosphites (Nos. 63, 64, 65, 66, 67, table 2), 12.02, and division of the remainder by 3, gives 0.96 for sodium light. The mean value of the atomic refractivity of oxygen in the $\equiv C—O—P\equiv$group is given in table 4, viz., 0.98 for D light on the Lorenz-Lorentz notation, and 1.38 for that of Gladstone-Dale.

(f) The value of the atomic refractivity of oxygen linked by a semipolar bond to phosphorus, $\equiv P\rightarrow O$, may be obtained by the following considerations:

(1) Subtraction of the molecular refractivity of phosphorus trichloride (No. 7, table 1) from that of phosphoryl chloride (No. 10) gives −1.13 for D light.

(2) Subtraction of the mean group refractivity for PO_3 in trialkyl phosphites (Nos. 63, 64, 65, 66, 67, table 2) from that for PO_4 in trialkyl phosphates (Nos. 73, 74, 75, 76, 77, 78, 79, 80, 81, 82) gives −1.15.

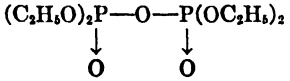
(3) Subtraction of the molecular refractivity of



$$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—P(OC_2H_5)_2$$

(No. 69, table 1)

from that of



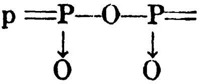
$$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}(OC_2H_5)_2$$

(No. 70)

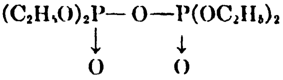
gives −0.38, not in good agreement with the values obtained above.

The mean of (1) and (2) gives −1.15 as the atomic refractivity of oxygen in the $\equiv P\rightarrow O$ group for D light. The corresponding Gladstone-Dale refractivity is −2.13.

(g) The value of the atomic refractivity of the covalent oxygen in the group $=\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}=$ may be obtained in the following manner:



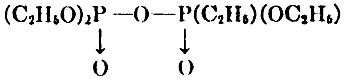
(1) Subtraction of the increments due to carbon, hydrogen, phosphorus [(a)] and the oxygen [(e) and (f)] from the molecular refractivity of



$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}(OC_2H_5)_2$ (No 70, table 1)

which gives the value 1.04 for sodium light.

(2) Similar consideration of the compound

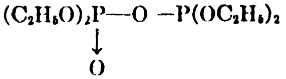


$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ O}}{P}(C_2H_5)(OC_2H_5)$ (No 72)

gives 0.95.

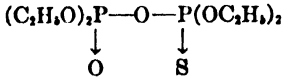
(h) The optical effect of sulfur joined by a coordinate link to phosphorus may be calculated as follows:

(1) Deduction of the molecular refractivity of



$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—P(OC_2H_5)_2$ (No. 69, table 1)

from that of



$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ S}}{P}(OC_2H_5)_2$ (No. 71)

leaves the value 6.69 for D light.

(2) The value obtained by subtracting the mean value of the group refractivity for PO_3 from that for PO_3S (No. 83, table 2) is 6.03.

(3) Subtraction of Eisenlohr's values for carbon and hydrogen, that for phosphorus given in (a), and that for oxygen in (e), in (f) and in (g), from the molecular refractivity of

$(C_2H_5O)_2\underset{\substack{\downarrow\\ O}}{P}—O—\underset{\substack{\downarrow\\ S}}{P}(OC_2H_5)_2$ (No. 71)

leaves the value 5.96.

The mean value of the Lorenz-Lorentz atomic refractivity of sulfur in the $\equiv P \rightarrow S$ group for D light is 6.23; the Gladstone-Dale, 11.43.

(j) Deduction of Eisenlohr's values for carbon and hydrogen, the present values for phosphorus given in (a), and for oxygen given in (e) and (f), from the molecular refractivity of

$$(CH_3S)(CH_3O)_2P\rightarrow O \text{ (No. 84, table 1)}$$

gives 7.49 as the value of the atomic refractivity of covalent sulfur in the group $\equiv C-S-P=$; that for the Gladstone-Dale formulation is 14.22, for sodium light.

TABLE 4

Mean values of atomic refractivities in phosphorus compounds on the assumption that the atomic refractivity of phosphorus is constant

ATOM	GLADSTONE-DALE			LORENZ-LORENTZ		
	F	D	C	F	D	C
P	14 65	14 23	13 75	9 33	9 14	9 00
O in $\equiv C-O-P=$	1 24	1 38	1 37	0 96	0 98	0 97
O in $\equiv P\rightarrow O$	−2 26	−2 13	−1 92	−1 25	−1 15	−1 05
O in $=\underset{\underset{O}{\downarrow}}{P}-O-\underset{\underset{O}{\downarrow}}{P}=$	—	3 31	—	—	1 00	—
S in $=P\rightarrow S$	—	11 43	11 81	—	6 23	6 01
S in $\equiv C-S-P=$	—	14 22	14 32	—	7 49	7 46
Cl	—	10 21	10 13	—	5 71	5 69

TABLE 5

Mean values of the atomic refractivity of phosphorus in various classes of compounds

	GLADSTONE-DALE			LORENZ-LORENTZ		
	F	D	C	F	D	C
Trialkylphosphines	14 65	14 23	13 75	9 33	9 14	9 00
Phenyldialkylphosphines	18 42	17 32	16 75	10 23	9 81	9 66
p-Tolyldialkylphosphines	19 21	17 93	17 45	10 65	10 20	10 03
p-Ethylphenyldialkylphosphines	19 90	18 56	18 06	10 89	10 40	10 23
p-Xylyldialkylphosphines	19 28	18 01	17 53	10 39	9 93	9 77
p-Methoxyphenyldialkylphosphines	20 11	18 64	18 08	10 93	10 39	10 19
p-Phenoxyphenyldialkylphosphines	22 45	20 51	19 75	10 47	9 83	9 58
Trialkyl orthophosphites	9 91	9 72	9 35	7 25	7 09	7 00
Trialkyl orthophosphates	4 96	4 85	4 72	4 36	4.39	4 32

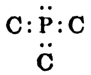
(k) Adding to the molecular refractivity of phosphorus trichloride (No. 7, table 1) the Eisenlohr values for alkyl groups and that for oxygen in the group $\equiv C-O-P=$, and subtracting from the sum the molecular refractivity of the corresponding alkoxydichlorophosphine (Nos. 55, 56, 57, 58, table 1), we obtain values for the atomic refractivity of chlorine attached to phosphorus; excluding the result for the methyl member (No.

54), the mean value is 5.71 for D light. For chlorine attached to carbon Eisenlohr gives 5.967. The mean Gladstone-Dale values are given in table 4.

Mean values are given in table 4, in the derivation of which the atomic refractivities of carbon and hydrogen given by Eisenlohr and those in table 3 have been employed, and, where necessary, suitable weighting has been applied for the sake of probable greater accuracy.

Up to this stage it has been assumed in this discussion that phosphorus possesses, independently of its state of combination, a constant atomic refractivity. The alternative view, however, must also be borne in mind, viz., that the atomic refractivity may have various values, dependent on the manner of the attachment of phosphorus to the other elements and on their character. For instance, assuming Eisenlohr's values for carbon, hydrogen, and ether oxygen, and that oxygen in phosphites and phosphates possesses the ether oxygen value, we can draw up a table (table 5) giving the various atomic refractivities of phosphorus.

The consideration of molecular refractivity as an additive property of bonds and of octets, rather than of atoms, has been brought forward by von Steiger, Fajans and Knorr, and Smyth (26). From this standpoint the value here obtained for the Lorenz-Lorentz atomic refractivity of phosphorus in tertiary phosphines, p, enables us to calculate the refractivity, $[R_0]$, of the octet



$$\begin{array}{c} \mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{P}}}:\mathrm{C} \\ \mathrm{C} \end{array}$$

Thus for D light,

$$[R_0]_D = \frac{3}{4}c + p = 10.954$$

wherein c denotes the atomic retractivity of carbon, given by Eisenlohr.

From what has been here stated it will be gathered that the refractive constants given in tables 4 and 5 and in the preceding paragraph must be looked upon not so much as possessing intrinsic theoretical significance, but as being of the nature of empirical constants whereby the molecular refractivity, and, therefore, also the refractive index, of a phosphorus compound may be determined when once its constitutional formula has been established. The converse use of these refractive constants to detect, for example, the presence of semipolar or of covalent bonds from refractometric measurements is obvious.

In conclusion it must be stated that, even in its modern form, the theory of the Mosotti-Clausius (27) equation, from which that of Lorenz-Lorentz and its limiting case, that of Gladstone-Dale, are theoretically derived, makes certain postulates regarding the mobility of the positive and negative charges in the molecule, and regarding the value of the constant of the inner field in the case of liquids (29), which are not strictly fulfilled. Moreover, the Maxwellian relation between dielectric constant and refractive index, assumed in the derivation of the Lorenz-Lorentz equation, holds only for electromagnetic oscillations of low frequency, that is, in regions far removed from absorption bands.

REFERENCES

(1) Kowalewski: J. Russ. Phys. Chem. Soc. **29**, 217 (1897).
(2) Haagen: Pogg. Ann. **131**, 119 (1867).
(3) Gladstone and Dale: Phil. Trans. **153**, 320 (1863).
(4) Gladstone: Proc. Roy. Soc. London **42**, 407 (1887).
(5) Zecchini. Gazz. chim. ital. **23**, 97 (1893); **24**, 34 (1894).
(6) Lorenz: Kgl. Danske Videnskab. Selskabs Skrifter **8**, 230 (1870); Wied. Ann. **11**, 70 (1880).
Lorentz: Wied. Ann. **9**, 641 (1880).
(7) Arbusow and Ivanow: J. Russ. Phys. Chem. Soc. **47**, 2015 (1915).
(8) Arbusow and Arbusow: J. prakt. Chem. **130**, 103 (1931); Ber. **65**, 197 (1932).
(9) Johnson: Ber. **65**, 302 (1932).
(10) Emmett and Jones: J. Chem. Soc. **99**, 714 (1911).
(11) Grüttner and Wiernik: Ber. **48**, 1473 (1915).
(12) Grüttner and Krause: Ber. **49**, 437 (1916).
(13) Jackson, Davies, and Jones: J. Chem. Soc. **1930**, 2300.
(14) Davies and Jones: J. Phys. Chem. **35**, 1490 (1931).
(15) Bowden: J. Soc. Chem. Ind. **49**, 257T (1930).
(16) Davies and Jones: J. Chem. Soc. **1929**, 33.
Davies, Pearse, and Jones: J. Chem. Soc. **1929**, 1262.
Evans, Davies, and Jones: J. Chem. Soc. **1930**, 1310.
Jackson, Davies, and Jones: J. Chem. Soc. **1930**, 2298.
Jackson and Jones: J. Chem. Soc. **1931**, 575.
Jackson, Davies, and Jones: J. Chem. Soc. **1931**, 2109.
(17) See J. Am. Chem. Soc. **54**, 1277 (1932).
(18) Bleekrode: Proc. Roy. Soc. London **37**, 339 (1884).
(19) Brühl: Z. physik. Chem. **7**, 19 (1894).
(20) Damien: Ann. École Norm. sup. **10** (1881).
(21) Thorpe and Tutton: J. Chem. Soc. **57**, 565 (1890).
(22) Martens: Verhandl. deut physik. Ges. **4**, 138 (1902).
(23) Nasini and Costa: Pubbl. dell 'Inst. chim. Roma, p. 111 (1891).
(24) Present work.
(25) Eisenlohr: Z. physik. Chem. **75**, 585 (1910).
(26) von Steiger: Ber. **54**, 1388 (1921).
Fajans and Knorr: Ber. **59**, 256 (1926).
Smyth: Phil. Mag. **50**, 361 (1925).
(27) Clausius: Mechanische Wärmetheorie, Vol. 2, p. 94 (1876).
(28) Brühl: Ber. **40**, 900, 1155 (1907).
Eisenlohr: Ber. **44**, 3188 (1911); Z. physik. Chem. **79**, 129 (1912).
(29) Loeb: Kinetic Theory of Gases, p. 397. McGraw-Hill Book Company, New York (1927).
Hückel: Theoretische Grundlagen der organischen Chemie, Bd. 2, p. 30. Akademische Verlagsgesellschaft, Leipzig (1931).

RECOVERY BY FLOTATION OF MINERAL PARTICLES OF COLLOIDAL SIZE

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In the early stages of the development of the flotation process for concentrating ores, the belief arose that at last a process of ore concentration was available for the successful treatment of the finest particles (1), which in water suspension are collectively known as "slime." It was thought that all mineral particles that are too fine to be recovered by gravity concentration and yet comprise a wide range of sizes float equally well. And, indeed, it is true that flotation is applicable to a wider size range than any of the three principal methods of gravity concentration — jigging, tabling, and vanning. Nevertheless the introduction of ball-mill grinding made it increasingly obvious that particles of all sizes do not float equally well or rapidly. The presence of an upper size limit beyond which flotation is impossible was recognized even before the advent of *selective* flotation (as contrasted with *collective* flotation). The existence of a lower size limit beyond which flotation is difficult was suspected, but the limitations of laboratory sizing technique made it difficult to more than surmise that particles of colloidal size are refractory to modern selective flotation operation (2).

Definite reduction in floatability with reduction in particle size beyond a critical size of maximum floatability was recently demonstrated (3). The size limits within which recovery by flotation is good were found to be more or less peculiar to each mineral. In general, however, the optimum size of mineral particles for concentration by flotation is between 50 and 10 microns, and the recovery is markedly lower for particles finer than 5 microns.

This dependence of flotation upon the size of particles was found to hold true in practical mill operations as well as in the flotation of synthetic mineral mixtures. About 10 per cent by weight of the ore treated in a modern mill is ground too fine to be recovered efficiently by flotation. The economic loss thus involved is appreciable.

It is therefore of considerable economic importance as well as of scientific interest to look into the possible causes for this behavior of fine particles and to devise, if possible, a more effective means of recovering them by flotation.

This paper deals with the study of the flotation behavior of exceedingly fine particles—those which in modern practice can be recovered only with difficulty.

The size range of these particles embraces the entire scale from 5 microns to the truly colloidal particles which have as their limiting size the unit crystal of the mineral (4).

In the size range considered the particles of near-colloidal size (5 to 0.5 microns) obey in kind, if not in degree, the same general laws of flocculation and dispersion (5) as the truly colloidal particles. Thus it is proper to examine and interpret the behavior of these fine particles in the light of colloid chemistry.

CAUSES FOR NON-FLOTATION OF COLLOIDAL PARTICLES

In the study of the effect of particle size on flotation a number of hypotheses were considered (3) to account for the non-flotation of particles of colloidal size. Of these hypotheses the most likely is that very fine particles do not float because it is difficult for them to come in contact with gas bubbles.

In recent years the emphasis laid upon the physicochemical properties of the mineral surfaces as determinants of flotation behavior have subordinated the equally important mechanical problem of bringing gas and solid together. The importance of gas–solid attachment is self-evident from a careful definition of flotation.[1]

Attachment of mineral particles to bubbles usually results from contact becoming established by direct encounter of particles with bubbles. It can be shown (6) that the probability of encounter between a mineral particle and a bubble varies directly as the size of the particle, provided the particle is small compared to the bubble. In other words, the finer the particle the poorer its chance of being recovered. Also, it appears likely that mineral recovery can be enhanced by flocculating the mineral.[2]

A further consideration, more directly deriving from customary colloid phenomena, also points to the desirability of flocculating the mineral which is to be floated. It is known that fine mineral particles suspended in an electrolyte are electrically charged (7); it is logically certain, furthermore, that the charge on particles of the same kind is of the same sign.

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[1] Flotation is a process of separation of mixed dissimilar solid particles, applied to the concentration of finely ground ores in aqueous pulp. The separation is caused by the selective adhesion of some species of solids to gas bubbles and the simultaneous adhesion of other species of solids to the aqueous solution; segregation of the resulting froth from the remaining pulp yields the desired separation.

[2] In this article the term "floccule" is used to describe an aggregation of solid particles suspended in a liquid in the absence of gas bubbles. In flotation literature the term "flocculation" has been used by some to refer to the formation of highly mineralized gas-solid aggregates. This confusing terminology is regrettable.

Accordingly, if it is proposed to cause electrically charged (dispersed) particles to adhere to a somewhat mineralized gas bubble, it should be expected that the mineral particles already attached to the bubble will prevent the adherence of more particles (8) and, hence, will prevent the formation of highly mineralized bubbles. Since flocculation in conducting media usually involves neutralization or great reduction of the charges responsible for dispersion, flocculation of the mineral may help flotation by eliminating or decreasing the electric charge at the surface of the particles.

From these considerations of the mechanics of gas–solid attachment, it seems likely that if fine particles can be made to lose their identity as such by coalescing into floccules, they may be expected to behave as coarse, uncharged particles, that is, to be more readily recovered by flotation.

MINERAL FLOCCULATION

The obvious means of flocculating a dispersed solid suspended in an electrolyte is to add to the electrolyte suitable soluble salts capable of discharging the dispersed phase.

Another means of flocculating the mineral is to form an insoluble heteropolar coating on the surface of the mineral, oriented in such a way as to make the transition from one phase to another abrupt (9). This is suggested by the following considerations. Dispersion can result either if the two phases are of like polarity or if there is established between them an intermediate zone or atmosphere of molecules or ions which is of a polarity intermediate between that of the two phases, so that a gradual transition is set up. Conversely, if the phases are very dissimilar, or if a film can be caused to develop on the solid, of a vastly different polarity than the liquid, the transition between the film-coated solid and the liquid will be abrupt and flocculation will tend to occur. Some of the experimental vindication for this argument is as follows:

H. E. Kamprath (10) studied the behavior of polar and non-polar minerals in polar and non-polar liquids. He found, for example, that silicate minerals, which are polar, flocculate in a non-polar liquid, but that in a heteropolar, nonconducting liquid they remain dispersed. One of the heteropolar liquids used was butyl alcohol, in which dispersion can hardly be attributed to electric charges. It would appear as though butyl alcohol molecules adhere to the solid in definite orientation so as to cause the surface of the coated silicate particles to have the same polarity as the liquid. That dispersion can be obtained under certain conditions without the presence of substantial electric charges was recently confirmed by Basil C. Soyenkoff (11), who concluded that "... the majority of colloid dispersions in hydrocarbons either are uncharged or carry only a small fraction (less than 10^{-4}) of the charge possessed by the particles in water."

Kamprath also found that graphite, which is non-polar, flocculates in polar liquids, but remains dispersed in non-polar liquids. The same behavior was noticed in the case of galena, provided it is kept from oxidizing. Thus, when galena is ground in water in a nitrogen atmosphere, it flocculates invariably, which may be considered to derive from its low polarity as compared with water.

EFFECT OF FLOCCULATION BY USE OF ELECTROLYTES ON FLOTATION OF GALENA

In order to ascertain the effect of flocculation by electrolytes on flotation it was thought wise to study extensively a simple system whose normal behavior is otherwise well known. Accordingly, mixtures of pure galena with granite (Butte quartz monzonite) were ground wet, long enough (twenty-four hours) to reduce all particles to 5 microns and finer. Various electrolytes were added to the pulp, after grinding, in the hope of improving flotation under standard conditions (12) (2.0 lb. of potassium amyl xanthate and 0.16 lb. of terpineol per ton). None of the substances investigated (lime, sodium hydroxide, aluminum sulfate, sodium carbonate) improved the recovery, although flocculation was obtained in many instances.

To study the problem further, galena and granite were ground separately for the time required to insure sufficient reduction in size, flocculating agents were added, the pulps were mixed, and flotation operations were conducted. Potassium *n*-amyl xanthate (2 to 4 lb. per ton) was used as collector, and terpineol (0.04 to 0.16 lb. per ton) as frother. The experiments showed that suitable flocculation of the mineral actually permits flotation of extremely fine mineral particles. Thus, if fine galena be first completely flocculated and then mixed with gangue minerals, an effective separation by flotation may be obtained. On the contrary, if the mineral be first completely dispersed and then mixed with gangue, recovery of the mineral is decidedly poor.

These experiments, however, do not simulate practice, as the sulfide and gangue minerals were ground separately, and flocculated (or dispersed) separately, so that the minerals exercised minimum influence on each other's behavior and that the system perhaps had not time to come to equilibrium. However, the experiments yield the valuable information that fine mineral particles are capable of ready attachment to bubbles if flocculated.

To apply this important experimental result to practice, care would have to be exercised to flocculate *selectively* the mineral to be floated, or else compound floccules of mineral and gangue would result. Such compound floccules would of course be a hindrance rather than a help to the separation of the minerals from each other. Thus, of the four possible states of aggregation of the minerals, that of flocculation of the mineral, together with dispersion of the gangue, is the most desirable. The other three, of course, are dispersion of mineral with dispersion of gangue, dispersion of mineral with flocculation of gangue, and flocculation of mineral with flocculation of gangue.

However, if the mineral and the gangue are ground together it is difficult to obtain simultaneously satisfactory flocculation of the sulfide and dispersion of the gangue. Dissimilar mineral particles tend to precipitate on the surface of one another (13), possibly because of the occurrence of unlike charges at their surfaces. Thus, some fine galena adheres to the surface of relatively coarse quartz, and, conversely, quartz adheres to galena. This phenomenon appears to take place in the grinding mill as soon as particles are formed fine enough to be affected by the charges that obtain at their surface. Hence, in order to prevent this action, it appears necessary to have present at the time when the fine particles are produced the agency that will cause the desired selective flocculation; that is, the selectively flocculating agent should be present in the grinding mill during the grinding.

TABLE 1

Comparison between amyl xanthate and amyl dixanthogen as collectors for colloidal galena

	XANTHATE	DIXANTHOGEN
Time of grind (hours)	24	30
Place of addition of reagent	Flotation machine	Pebble mill
Quantity of reagent (pounds per ton)	4.0	3.0
Time required for rougher flotation (minutes)	60	5
Rougher concentrate (lead, per cent)	43.1	39.3
Tailing (lead, per cent)	4.4	0.30
Lead recovery (per cent)	80.5	98.7
Rougher selectivity index* Lead Granite	4.0	15.5
Cleaner concentrate (lead, per cent)		69.4
Cleaner tailing (lead, per cent)		1.10

* For method of calculation see A. M. Gaudin: Flotation, p. 526 (see reference 5).

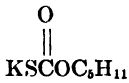
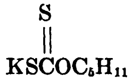
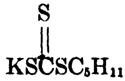
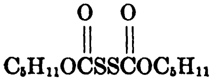
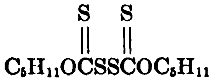
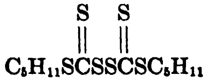
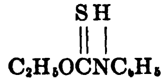
The search for a means to cause simultaneously the selective flocculation of the sulfide mineral and the dispersion of the gangue by the use of electrolytes was abandoned after much experimentation because the action of electrolytes did not appear to be selective enough.

FLOCCULATION AND FLOTATION OF COLLOIDAL SULFIDE MINERALS, USING CERTAIN SULFUR-BEARING HETEROPOLAR COMPOUNDS

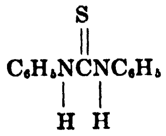
Remarkably successful flotation of colloidal sulfide minerals may be obtained by the use of certain heteropolar organic compounds. These compounds have a structure such as to make possible the formation of oriented coatings of molecular dimensions on the sulfide minerals, and thereby produce selective flocculation of the sulfide minerals. This is true provided the flocculating-floating compounds are added to the mineral mixture before grinding.

In this connection it should be stated that in the experiments discussed in the preceding section a sulfur-bearing heteropolar compound was used in each test as a flotation collector. The reagent used was potassium *n*-amyl xanthate, a reagent known to be exceptionally effective in the flotation of coarse sulfide minerals. Nevertheless, under normal conditions this compound is not capable of floating slimed galena. On the contrary, *n*-amyl dixanthogen, a non-ionized oxidation product of *n*-amyl xanthate, under certain conditions is capable of recovering colloidal galena. This discovery led to a broadening of the investigation to include non-ionized as well as ionized organic compounds containing single- or double-bonded sulfur atoms and an amyl, a phenyl, or a cresyl hydrocarbon group.

Some of the reagents investigated and their formulas are as follows:

Potassium *n*-amyl thiocarbonate .. .	 $KS\overset{\overset{O}{\|}}{C}OC_5H_{11}$
Potassium *n*-amyl dithiocarbonate (xanthate)	 $KS\overset{\overset{S}{\|}}{C}OC_5H_{11}$
Potassium isoamyl trithiocarbonate .	 $KS\overset{\overset{S}{\|}}{C}SC_5H_{11}$
n-Amyl formate disulfide	 $C_5H_{11}O\overset{\overset{O}{\|}}{C}SS\overset{\overset{O}{\|}}{C}OC_5H_{11}$
n-Amyl thioformate disulfide (dixanthogen)	 $C_5H_{11}O\overset{\overset{S}{\|}}{C}SS\overset{\overset{S}{\|}}{C}OC_5H_{11}$
Isoamyl dithioformate disulfide	 $C_5H_{11}S\overset{\overset{S}{\|}}{C}SS\overset{\overset{S}{\|}}{C}SC_5H_{11}$
Isoamyl disulfide	$C_5H_{11}SSC_5H_{11}$
Isoamyl sulfide	$C_5H_{11}SC_5H_{11}$
Isoamyl mercaptan	$C_5H_{11}SH$
p-Thiocresol	$HSC_6H_4CH_3$
Phenyl thiourethane	 $C_2H_5O\overset{\overset{S}{\|}}{C}\overset{\overset{H}{\vert}}{N}C_6H_5$

Thiocarbanilide.



$$C_6H_5\underset{\underset{H}{|}}{N}\overset{\overset{S}{\|}}{C}\underset{\underset{H}{|}}{N}C_6H_5$$

Tri-*o*-cresyl thiophosphate $(C_6H_4CH_3O)_3PS$

Of the above, the first six belong to a group of which xanthate and dixanthogen are representative. The compounds in this group other than the xanthate and dixanthogen were especially prepared in order to clarify the mechanism of attachment of the compound to the mineral. For this reason the double-bonded, or thione, sulfur atoms in xanthates and dixanthogen, which are commonly regarded by flotation engineers as being at least partly responsible for the attachment of minerals to bubbles, were replaced by oxygen atoms to form formate disulfide and potassium thiocarbonate; also, the oxygen atoms were entirely eliminated by replacing them with sulfur atoms in the case of dithioformate disulfide and potassium trithiocarbonate.

With the exception of the potassium salts, the compounds enumerated are but sparingly soluble in water, but since the organic solvents necessary to dissolve the agents may interfere in an undetermined manner with flotation, the undiluted agents were added directly to the grinding mill so as to be in intimate contact with the mineral throughout the grinding operation.

Flotation was conducted in a 500-g. Fahrenwald flotation machine. The products were analyzed for the valuable metal content. A flotation operation was arbitrarily termed successful when the tailing assayed less than 0.5 per cent (in valuable metal), and if the recovery exceeded 96 per cent. (Ordinarily, flotation under standard conditions, with the reagents added after grinding, yields a tailing having a metal content exceeding 3 per cent). It was found unnecessary to use any frother in most of the flotation operations.

The mineral mixtures were ground in porcelain jars ("assay" pebble mills) long enough to be reduced to the near-colloidal size. Investigation was confined to five of the commonest mineral sulfides (galena, chalcocite, chalcopyrite, pyrite, and sphalerite) and to the gangue minerals occurring in quartz monzonite (quartz, andesine, magnetite, biotite, hornblende). The grinding was conducted in contact with air in the case of every reagent and of every mineral mixture. Identical tests, except for grinding in contact with nitrogen, were also conducted. The tests in which the minerals were ground in nitrogen were undertaken to supply some information concerning the very peculiar behavior of some mineral-reagent combinations. It is well known that sulfide minerals are readily oxidized. It has been currently assumed (14) that surface oxidation of sulfide minerals is prerequisite for modern flotation. Obviously, even in the case of particles ground in the presence of a restricted amount of oxygen —as in the tests under consideration—much oxidation may take place during a period of grinding of many hours. Also, change in the reagent may take place when the reagent is added so as to be in contact with a mineral and air for many hours during grinding. Clearly, when the mineral is ground in the presence of nitrogen, such reactions are largely inhibited and the reagent then acts on relatively unchanged sulfide surfaces.

Table 2 summarizes the floatability of the different minerals with some of the more effective agents.

Flotation of colloidal sphalerite can be accomplished by none of the reagents listed, unless, of course, the mineral is first activated.[3]

Of the compounds which are similar in structure to amyl xanthate and dixanthogen (thioformate disulfide), namely, the thiocarbonate, trithiocarbonate, formate disulfide, and dithioformate disulfide, none showed any great promise to collect colloidal galena. The formate disulfide showed some tendency to collect galena, but it was too weak to be considered satisfactory. The action of these substances on other minerals was not investigated.

TABLE 2

Flotation of slimed sulfide minerals ground in contact with air when using some heteropolar sulfur-bearing compounds

	GALENA	CHALCOCITE	CHALCOPYRITE	PYRITE
Potassium amyl xanthate	Fair	Good	Good	Good
Amyl dixanthogen	Good	Good	Good	Good
Isoamyl disulfide.	None	Good	Fair	None
Isoamyl sulfide	None	None	Good	None
Isoamyl mercaptan	None	Good	Good	—
Thiocresol	None	Good		—
Phenyl thiourethane	Good	None	—	—

Isoamyl disulfide was effective for chalcocite only.

Isoamyl sulfide promoted the flotation of chalcocite and pyrite only when these minerals were ground in nitrogen. Its effect was nil when the minerals were ground in air. It was effective for flotation of chalcopyrite irrespective of the atmosphere in which the mineral was ground.

Isoamyl mercaptan was effective only for chalcocite and chalcopyrite. Its action on the flotation of galena and sphalerite was nil. Its action on pyrite was not investigated.,

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[3] By activation is meant the formation on the surface of the mineral of a layer which will react with the collector to which the unactivated mineral surface fails to respond.

Thiocresol exhibited good collecting properties in the case of chalcocite, but none at all in the case of galena and sphalerite. Its action on other minerals was not studied.

The experimental results related above give little grounds from which sweeping generalizations can be drawn for predicting the action of the same compound on different minerals, or for designating a definite compound as one likely to be effective in promoting selective slime flocculation and the collection of floccules in flotation. In the present state of our knowledge, all that can be said is that the action of a given compound seems, to a large extent, to be specific to each mineral. It is hoped, however, that significant broad conclusions will be possible following the experimentation now in course.

DRY VERSUS WET FROTHS

During the investigation with the organic compounds as selective flocculators a curious phenomenon was observed: in the case of some of the reagents a peculiar "dry" froth was obtained in the flotation operation. This unusual type of froth occurred if an amount of agent greater than a certain critical amount was used; when the amount of the agent used was less than this critical amount, the froth had the normal or "wet" appearance. The "dry" froth contains very little interbubble water and is in the form of a thick, dry mass which is made up of extremely fine bubbles, difficultly distinguishable by eye. Whenever a dry froth was obtained, most of the mineral floated in the dry mass in one minute, whereas flotation of colloidal material with the usual wet froth requires twenty minutes or longer. What mineral did not float in the dry froth came up in the form of a dull dry film, which formed persistently at the surface of the pulp for some time and which had to be raked off painstakingly. This remainder could not be induced to float in the form of a froth even with the addition of large amounts of frother. By the use of reagents giving the usual type of froth, a good recovery of colloidal mineral in the cleaning operation is always difficult, but whenever a dry froth is obtained the cleaner tailing is but slightly higher in metal content than the rougher tailing. Moreover, owing to the dry character of the dry froth, the concentrate obtained is very clean, devoid of the usual adulterating interbubble gangue suspension. Most of the froth remained indefinitely in the dry condition, resembling stiff whipped cream in plasticity. The small part that did disintegrate settled to the bottom of the water layer in very large floccules. Instead of cleaning the rougher concentrate by flotation, therefore, simply draining or filtering off the water (containing dispersed gangue suspension) could be used as a substitute.

Wet froths obtained by the use of heteropolar reagents were examined to determine whether the mineral floats in the form of floccules or whether it floats as dispersed mineral particles attached to gas bubbles. Samples of froth were dried, then pieces were broken off and the thickness of the bubble wall was measured. This thickness was found to vary between 4 and 7 microns. The dried bubble was then broken up, and the individual particles in it were likewise measured after dispersion in pure terpineol. Most of the particles were smaller than half a micron. From a microscope examination of slides of the pulp, the diameter of the average floccular unit of the mineral was determined to be in the neighborhood of 4 to 7 microns. Hence, it appears that the bubbles in the froth are made up of the same floccules that occur in the pulp. Similar determinations could not be obtained with dry froths because of the minuteness of the bubbles. From the partial disintegration of dry froths to form very coarse floccules, and from their dull luster it appears likely that they consist of floccules even larger than those occurring in wet froths.

It was observed that coarse floccules float before finer flccules, a sequence analogous to that observed for the flotation of dispersed particles (3).

SUMMARY

1. Hypotheses were considered to account for the non-flotation of colloidal particles. It is believed that non-flotation of colloidal sulfide mineral particles is due to their being unable to come in contact with gas bubbles because of fine size and state of dispersion.

2. Selective flocculation of colloidal mineral makes its flotation more complete and easier.

3. Owing to the possibility of mutual flocculation of fine gangue and sulfide minerals in a flotation pulp, it appears necessary, in order to effect selective flocculation, to act on the mineral particles at the time they are produced in the grinding operation.

4. Flotation of colloidal sulfide mineral particles may be successfully accomplished by using as reagents certain heteropolar sulfur-bearing organic substances. These agents effect selective flocculation of the sulfide mineral particles.

REFERENCES

(1) Megraw, H. A.: The Flotation Process, p. 157. McGraw-Hill Book Co., New York (1916).

(2) Megraw, H. A.: The Flotation Process, pp. 28, 143.

Hoover, T. J.: Concentrating Ores by Flotation, p. 158. Mining Mag., London (1912).

Taggart, A. F.: Handbook of Ore-Dressing, p. 859. Wiley and Sons, New York (1927).

(3) Gaudin, A. M., Groh, J. O., and Henderson, H. B.: Am. Inst. Mining Met. Engrs., Tech. Pub. 414 (1931). Effect of Particle Size on Flotation.

Brunner, J. J.: Effect of Particle Size on Flotation; Part II Master of Science Thesis, Montana School of Mines.

(4) Gross, J , and Zimmerley, S R Am Inst Mining Met Engrs , Milling Methods, p 30 (1930) Crushing and Grinding, II —Relation of Measured Surface of Crushed Quartz to Sieve Sizes

(5) Gaudin, A M Flotation, pp 44–9 McGraw-Hill Book Co , New York (1932)

(6) Gaudin, A M Flotation, pp 88–90

(7) Ince, C R Am Inst Mining Met Engrs , Milling Methods, p 261 (1930) A Study of Differential Flotation

Callow, J M Mining Sci Press **111**, 854 (1915) Notes on Flotation Kolloidchem Beihefte **2**, 84 (1914), Z physik Chem **89**, 91 (1914)

(8) Taylor, N W Trans Electrochem Soc **60**, 305 (1931) Discussion of "An Outline of Some Physicochemical Problems of Flotation" by A M Gaudin

(9) McBain, J W Colloid Symposium Monograph IV, 7 (1926) A Survey of the Main Principles of Colloid Science

Fahrenwald, A W Trans Electrochem Soc **60**, 311 (1931) Solubility, Peptization, Wetting and Flotation

(10) Kamprath, H E A Study of the Dispersion and Flocculation of Pure Mineral Suspensions in Liquids Master of Science Thesis, Montana School of Mines, 1931

(11) Soyenkoff, Basil C J Phys Chem **34**, 2519 (1930) Benzene Dispersions of Basic Soaps of Nickel and Iron J Phys Chem **35**, 2993 (1931) Hydrocarbons as Dispersion Media A Review

(12) Groh, J O , and Henderson, H B Effect of Particle Size on Flotation Master of Science Thesis, Montana School of Mines

(13) Taggart, A F Taylor, T C and Ince, C R Am Inst Mining Met Engrs , Milling Methods, p 285 (1930) Experiments with Flotation Reagents

(14) Taggart, A F , Taylor, T C , and Knoll, A F Am Inst Mining Met Engrs Milling Methods, p 217 (1930) Chemical Reactions in Flotation

THE PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. II

THE FREEZING POINTS OF SOME OF THE THERMOMETER CALIBRATION STANDARDS FOR LOW TEMPERATURES OF THE BUREAU INTERNATIONAL DES ETALONS PHYSICO-CHIMIQUES[1]

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In the course of another investigation requiring a careful thermocouple calibration at low temperatures, accurate freezing point determinations were made on a number of samples of organic compounds supplied "for thermometer calibration" by the Bureau International des Etalons Physico-Chimiques, University of Brussels, in order to add to the certainty of our temperature scale and also to prove that our method of determining freezing points by means of heating curves is satisfactory and has advantages over the usual methods. The freezing point values attributed to these samples were based upon measurements made by Professor Timmermans against the helium thermometer of the Laboratoire Cryogénique de l'Université de Leiden in 1922 (1) and repeated in 1928 (2), when slightly different values were assigned to chlorobenzene, carbon disulfide, and methylcyclohexane.

Our freezing point measurements were made by means of a method particularly adapted to the accurate determination of this physical constant at low temperatures. We believe, therefore, that the results may help to establish definitely the true freezing points of these samples. The "accepted values" of Timmermans are identical with ours within the claimed limits of accuracy except in two cases, and in both of these cases we have been able to show that his values published in 1922 are more nearly correct than those he assigned to them on the basis of his 1928 determinations.[3]

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[1] Contribution No. 258 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts. A part of the experimental work for this paper was completed at Trinity College, Hartford, Connecticut, thanks to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and to Curtis H. Veeder of Hartford, for grants to defray the expenses, and also to the Yale University Physics Department for supplying the necessary liquid air at cost.

[2] National Research Fellow, 1926–28, at the Massachusetts Institute of Technology; Guggenheim Fellow, 1930–31, at the Universities of Munich, Frankfurt a. Main, and Brussels.

METHOD

The observations here reported were made by means of a cooling-curve and heating-curve apparatus which is being described in detail elsewhere (3). This apparatus involves a cryostat whose temperature can be very carefully regulated and in which a 0.5 – 1.0 g. sample is suspended in an hermetically sealed "freezing point tube." The latter is made of extremely thin-walled 6-mm. glass tubing (about 0.08-mm. wall thickness) in order that its heat capacity may be negligibly small with respect to that of the sample, and is so constructed that the temperature of the sample may be followed by means of a single-junction thermocouple, one element of which fits snugly into a thin-walled capillary tube extending down through the center of the tube to within 5 mm. of the bottom. The cold junction is kept at 0°C. The readings are made to the nearest microvolt by means of a Leeds and Northrup Type K potentiometer.

The freezing point is determined by running heating curves and cooling curves on the sample, always controlling the temperature of the surroundings to rise or fall, as the case may be, at a definite recorded rate. The reproducibility of the curves so obtained, their interpretation, and the advantages of heating curves over cooling curves for the determination of freezing point and also as a criterion of purity have already been pointed out (3).

Since the thermocouple calibration was only to the nearest microvolt (±0.02°C., at 0°C., to ±0.05°C. at liquid air temperature), and since our freezing point values are also read only to the nearest microvolt, our freezing points cannot be said to have an accuracy greater than ±0.04°C. at 0°C., to ±0.10°C. at −183°C.

THERMOCOUPLE CALIBRATION

Five different thermocouples, made of No. 30 constantan and No. 36 copper wire, were used. Two of these were calibrated simultaneously at the ice point, at the freezing point of mercury (−38.87°C.) (4), at the sublimation point of carbon dioxide (−78.51°C.) (4), and at the boiling point of oxygen (−183.00°C.) (4). The last two points were established by measuring the vapor pressure of the carefully purified substances in a constant temperature cryostat in which the thermocouple was immersed (5). In each case the purity of the sample was tested by evaporating to one-half volume and then redetermining the vapor pressure. The calibration at the mercury point was carried out in the same apparatus as the freezing points and under identical conditions.

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[3] In order to clear up a misunderstanding in regard to the samples prepared by R. S. Taylor, and studied by Keyes, Townshend, and Young (J. Math. Phys. Mass. Inst. Tech. **1**, 302 (1922)), which have been criticized by Timmermans, it should be pointed out that the sole claim made by these authors was as follows: "The freezing point found for an organic liquid depends somewhat upon the method employed and the thoroughness of the purification. The results here given will be found reproducible provided the general method of procedure is followed." In a letter to the author Professor Keyes states: "The use to which these samples were put was in connection with the production of helium in Texas. Whether the samples were of the highest purity or not made little difference in this connection, since they served to transfer temperature indications obtained from my hydrogen thermometer and platinum resistance thermometers to the operators at the Texas helium plant."

The other three thermocouples were calibrated against these two, all being inserted simultaneously in a constant temperature bath of pentane, the cryostat described by Taylor and Smith (6), and all five being read several times in rotation while the temperature of the cryostat was kept constant at various temperatures at intervals of about ten degrees along the scale, until at least three consecutive series of readings at each temperature gave identical values.

MATERIALS

Samples of the following compounds were obtained from Professor Timmermans, Director of the Bureau International des Etalons Physico-Chimiques: carbon tetrachloride, chlorobenzene, chloroform, ethyl acetate, carbon disulfide, ethyl ether, and methylcyclohexane, each in a tube sealed *in vacuo.* Each sample was introduced without further treatment into a freezing point tube with the minimum possible exposure to the atmosphere and was sealed off by the usual procedure without evacuating. Though the samples may not have been identical with those used by him in his freezing point determinations, they were similarly purified, and had the same densities within ±.0001 in all cases (7).

RESULTS

A number of heating and cooling curves were run on each substance at various intervals in the course of eighteen months, employing more than one thermocouple for each sample. The samples were always kept in a dark cupboard between measurements.

With the exception of ethyl acetate and methylcyclohexane, the values accepted for the freezing points are based on both heating and cooling curves. In all these cases all except the highest, cooling curve values were rejected, since obviously the effect of an unsatisfactory degree of supercooling, or of a failure to reach true equilibrium between the solid and liquid phases, is to give a freezing point which is too low. This was an important factor only in the case of the ethyl ether sample, where the highest cooling curve values agreed satisfactorily with the heating curve values, but where many cooling curves gave values from two to four microvolts lower. It was not found possible to measure the freezing points of the ethyl acetate and methylcyclohexane by our cooling curve method; all the values so obtained were not only low but inconsistent. This was particularly true for the methylcyclohexane. The best value obtained for the ethyl acetate, for example, was −83.84°C. Thus, the advantage of the heating curve method was particularly evident in these cases.

The stable form of ethyl ether was the one most often obtained by cooling curves, though a preliminary halt of five to twenty seconds at the freezing point of the unstable form was usually noted. It seems possible that crystals of the unstable form always appear first in accordance with Ostwald's step-by-step theory (8). It should also be mentioned that our experiments showed definitely that transition from the unstable to the stable form of ether can take place completely in the solid phase. This was proved by the fact that heating curves for the stable form were obtained on samples which had solidified completely as the unstable form as shown by the complete cooling curves.[4]

TABLE 1

Freezing points of Timmermans' thermometer standards

SUBSTANCE	TIMMERMANS' VALUES				FREEZING POINT (SKAU)	DIFFERENCE FROM ACCEPTED VALUE
	On label	(1922)	(1928)	Accepted value (1928)		
	degrees C	*degrees C*	*degrees C*	*degrees C*	*degrees C*	*degrees C*
Carbon tetrachloride*.	−22 9	−22 894	−22 82	−22 85	−22 8^{6}	+0 01
Chlorobenzene	−45 2	−45 175 −45 382	−45 35	−45 35	−45 2^{2}	−0 13
Chloroform	−63 5	−63 495	—	−63 5	−63 4^{1}	−0 09
Ethyl acetate	−83 6	−83 6	—	−83 6	−83 6^{3}	+0 03
Carbon disulfide	−111 6	−111 613	−111 84	−111 8	−111 8^{8}	+0 08 (0 04)
Ethyl ether (stable).	−116 3	−116 322	−116 35 −116 37	(−116 3)†	−116 2^{9}	−0 01
Ethyl ether (unstable)	−123 3	−123 301	−123 47 −123 50	−123 3	−123 2^{5}	−0 05
Methylcyclohexane.	−126 3	−126 35	−126 85	−126 85	−126 3^{4}	−0 51

* The transition point of carbon tetrachloride was also determined on this same sample. Transition point = −47.55 ±0 12°C.; see Skau and Meier: J. Am. Chem. Soc. **51**, 3517 (1929).

† Private communication.

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[4] The behavior of ether here described has a bearing on a statement made by Smits (Z. physik. Chem. **153A**, 287 (1931)): "Der Umwandlungspunkt der flussigen Phase liegt bei −105.4° und weiterhin kennt man zwei Schmelzpunkte bei −116° und bei −123.4°. Die Modifikation mit dem niedrigsten Schmelzpunkt, die am leichtesten erhältlich ist, hat man bisher als die metastabile Modifikation betrachtet. Da man

In no case was there found to be an appreciable change in freezing point with time, though the determinations were carried out over the course of about eighteen months using the original samples throughout. This brings out another advantage of our freezing point method for, as has been pointed out by Timmermans (9), pure chloroform, for example, is very sensitive on exposure to the air.[5]

The results have been summarized in table 1. Column 2 shows the freezing point values given on the labels of the sample tubes as received; columns 3 and 4 give Timmermans' Leiden values of 1922 and 1928 respectively; column 7 shows the differences between our values, column 6, and the final accepted values of Timmermans, column 5.

Since the accuracy claimed by Timmermans for his freezing points is only 0.1°C., all of our values can be said to check his final "accepted values," with the exception of that for methylcyclohexane and probably that for chlorobenzene. In both of these cases, however, our values agree very closely with those determined by him[6] in 1922. On the other hand, our value for carbon disulfide agrees with his more recent value, which was 0.23°C. lower than the value he reported in 1922.

It is suggested that the following be accepted as the freezing points of these substances[7] on the basis of the data now available:

Carbon tetrachloride	−22 8^{5}°C.
Chlorobenzene	−45 2^{0}
Chloroform	−63 4^{5}
Ethyl acetate	−83 6^{0}

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aber nunmehr weiss, dass die Flussigkeit allotrop ist, kann auch . . . die Modifikation mit dem hoherên Schmelzpunkt die metastabile Modifikation sein. Wir sind damit beschaftigt diese Frage experimentell zu klaren". Our results show that for ether the form with the lower melting point is the unstable form, which is, in fact, in agreement with more recent experiments by Smits (private communication).

[5] Professor Keyes suggests the desirability of designing a freezing point tube similar in construction to the one here described but with a larger capacity so that it could be used with a platinum resistance thermometer with a correspondingly modified technique. This could probably be used solely for the cooling-curve method, but would be decidedly advantageous in that (1) it would make available for temperature comparison a number of substances which crystallize well but which become impure on exposure to air, and (2) it would obviate the necessity of handling the sample before freezing point determinations, with the resulting possibility of the introduction of impurities.

[6] The reason suggested by Professor Timmermans for the lowness of his value for the freezing point of methylcyclohexane in 1928 is that considerable air may have dissolved in the sample, for by his method the sample is stirred vigorously without excluding air (private communication).

[7] Professor Timmermans has expressed his willingness to endorse this revision of his "accepted values" in the light of the evidence now at hand (private communication).

Carbon disulfide	-111.8^{5}°C.
Ethyl ether (stable)	-116.3^{0}
Ethyl ether (unstable)	-123.3^{0}
Methylcyclohexane	-126.3^{5}

The values for toluene and isopentane, which also belong to this series but which, unfortunately, were not included here, will be determined at the earliest opportunity.

This investigation bears out the fact that accurate freezing points can be measured by heating curves. It should be pointed out that our method has the decided advantage of being applicable to all substances which can be caused to crystallize within the temperature range from 250°C. down to very low temperatures, irrespective of their viscosities or other properties, such as a slow rate of crystallization, which interfere with obtaining good values by the usual cooling-curve or Beckmann method (3). It requires only a small sample, an important factor where rare substances are being dealt with, and any number of determinations can be made on the same sample. Most important, the sample can be introduced into the freezing point tube and sealed off entirely out of contact with air, and the determination made *in vacuo*. This is particularly important not only in the case of compounds which are hygroscopic (like ethyl alcohol), or which absorb carbon dioxide in contact with air (like polyphenols), but also in the case of any liquid freezing below 0°C., for at low temperatures the condensation of moisture and of carbon dioxide, as well as the dissolving of the other constituents of the atmosphere, are a very grave source of contamination.

REFERENCES

(1) Timmermans, Van der Horst, and Onnes: Arch. néerland. sci. IIIA, **6**, 180 (1922). See also: Communications Phys. Lab. Univ. Leiden, Suppl. 51b, p. 35 (1924).

(2) Timmermans: Communications Phys. Lab. Univ. Leiden, Suppl. 84, p. 3 (1928).

(3) Skau: Proc. Am. Acad. Arts Sci. **67**, 551 (1933).

(4) International Critical Tables, Vol. I, p. 53.

(5) Keyes, Townshend, and Young: J. Math. Phys. Mass. Inst. Tech. **1**, 302 (1922), for a full description of the details of this method. See also, Loomis and Walters: J. Am. Chem. Soc. **48**, 3101 (1926), and Henning: Ann. Physik **43**, 282 (1914).

(6) Taylor and Smith: J. Am. Chem. Soc. **44**, 2450 (1922).
Keyes, Taylor, and Smith: J. Math. Phys. Mass. Inst. Tech. **1**, 211 (1922).
See also, Cardoso: J. chim. phys. **15**, 317 (1915).

(7) Private communication.

(8) Ostwald: Z. physik. Chem. **22**, 306 (1897).

(9) Timmermans: Helv. Chim. Acta **14**, 445 (1931).

A NEW METHOD FOR THE PREPARATION OF OXIDE CATALYSTS FOR THE CARBON MONOXIDE OXIDATION[1]

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INTRODUCTION

The study of the catalytic oxidation of carbon monoxide was begun in 1917 as a result of the war gas investigations. At first, in view of the practical nature of the problem, attention was focused upon the preparation of some cheap and durable catalyst, efficient at temperatures as low as 0°C. As a result of these studies there were prepared commercial catalysts consisting of mixtures of oxides. The preparation of a single pure oxide in sufficiently active state to be 100 per cent efficient at low temperatures was first accomplished in the case of manganese dioxide (1). Later an equally active cobalt sesquioxide (2) was prepared. In 1930, Bennett and Frazer (3) made a thorough study of seventeen pure metallic oxides, of which oxides eleven were partially efficient below 200°C. and three were 100 per cent efficient at freezing temperatures. These three active catalysts were the oxides of manganese, cobalt, and nickel.

A survey of the above work emphasizes several requisites for an efficient catalyst: (1) It must be finely divided. Any heat treatment reduces the active surface by sintering and is thus detrimental to the efficiency of the catalyst. This was recognized at the beginning of the investigation, and precipitation methods have been used throughout. (2) An oxide of a single metal, in order to be an efficient catalyst, must be extremely pure. Traces of impurities may inhibit or even entirely destroy the activity of the oxide. The success of Bennett's oxide catalysts was largely dependent on his method of purification of the hydroxides by electrolytic filtration. In previous experiments, the finely divided state of the oxide has been invariably secured by precipitation methods, and purity of the oxide by washing. Precipitation did secure a finely divided oxide, but it invariably resulted in contamination of the catalyst by the precipitant, usually sodium hydroxide. Lengthy and tedious washing was depended upon to remove the impurity.

The low temperature oxidation of pyrophoric metals provides a means for the preparation of oxide catalysts whereby no impurity is introduced in large concentration and what foreign matter is present is easily removed. It is the purpose of this paper to develop in detail this new method for obtaining the oxides of nickel, cobalt, iron, manganese, and copper.

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[1] From the dissertation submitted by C. M. Loane to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Two procedures were used for the preparation of the finely divided, pyrophoric metals: (1) Preparation of the metallic amalgams and subsequent removal of the mercury by distillation (4); (2) Reduction of the metallic salt by sodium in ammonia solution (5).

PREPARATION OF OXIDES OF METALS FROM AMALGAMS

The metallic amalgams were prepared by electrolysis of a slightly acid solution of the sulfates over a mercury cathode. The amalgams were vacuum distilled and the metal obtained in a pyrophoric condition. After oxygen had gradually come in contact with the metal so that at no time was a larger amount of heat generated, the product was tested for its catalytic efficiency.

Since the oxides prepared by the above method were not washed before testing, care was taken to purify the mercury and the sulfates used in the electrolysis.

The mercury was passed through a 6-foot nitric acid column four times and distilled three times.

Chemically pure sulfates were twice recrystallized. The electrolysis was carried out in a 400-cc. beaker. The concentration of the salt was chosen so that, by complete electrolysis of 300 cc. of solution, an approximately 2 per cent amalgam would be obtained. A few drops of sulfuric acid were added to the solution so prepared. Thirty cubic centimeters of mercury formed the cathode in the bottom of the beaker. The anode was of platinum gauze, except in the case of the manganese and iron salts. A current of approximately one ampere was used, so that the electrolysis was generally completed in twenty-four hours. Excess electrolyte was removed by washing the amalgam with distilled water.

In the case of the electrolytic preparation of the iron amalgam, an iron wire anode was used instead of the platinum gauze.

If the usual platinum anode was used when preparing the manganese amalgam, the amalgam was contaminated by scales of manganese dioxide forming at the anode and falling down on the amalgam. This difficulty was overcome by enclosing the anode in a glass tube, the bottom of which was formed by a porous clay disc. The inside of the tube was filled with concentrated ammonium nitrate solution. With these precautions observed, the electrolysis proceeded smoothly, without the formation of any dioxide. However, owing to the porous disc between the electrodes, only a small current could pass, and a week was necessary before a sufficiently concentrated amalgam was obtained.

In table 1 are listed the results of the above procedures.

Another method of obtaining the oxide catalysts was also used. The concentrated amalgam was exposed to the air until sufficient metal had separated as the oxide, and the powder was mechanically separated. Oxides of cobalt and of iron were readily obtained in this way. Nickel and manganese oxides were obtained in sufficient quantity only after several months. Copper amalgam was stable, no apparent oxidation taking place.

TABLE 1

Metallic oxides prepared from amalgams

METAL	NATURE OF AMALGAM	DISTILLATION TEMPERATURE	NATURE OF METAL	CONDITIONS OF OXIDATION	NATURE OF OXIDE
		degrees C			
Nickel	Thick, smooth	190	Dull grey, fluffy mass	O_2 stream 2 hours at 200°C.	Grey
Cobalt ..	Lumpy	250	Hard, grey, metallic lump	O_2 stream 3 hours at 200°C.	Grey, metallic
Iron ..	Thick, lumpy	250	Hard, black lump	240°C 3 hours	Dark red
Manganese	Smooth, dilute	200	Grey, porous lump	200°C. 18 hours	Dark brown
Copper	Thick, lustrous	200	Red, spongy	200°C. 10 hours	Surface—dark blue

PREPARATION OF OXIDES OF METALS OBTAINED BY REDUCTION IN AMMONIA

Selected anhydrous salts of the metals were dissolved in ammonia and sodium added. The metals precipitated by the sodium were filtered, washed by ammonia, and allowed to oxidize slowly.

Anhydrous nitrates were used wherever possible. The nitrates cannot be dehydrated by heat treatment alone, for they decompose at a lower temperature than is necessary to drive off the water. A special method was necessary. That of Guntz and Martin (6) for the preparation of anhydrous cobalt and nickel nitrates seemed the most convenient. The nitrate was dissolved in its own water of crystallization at as low a temperature as possible and the solution poured into a large excess of fuming nitric acid. In several minutes the anhydrous salt precipitated. The excess nitric acid was decanted, and the precipitate washed several times with fuming nitric acid. Most of the acid was decanted and the rest removed by vacuum distillation over quicklime and phosphorus pentoxide. This procedure was successfully applied to the nitrates of nickel, cobalt, and copper.

Ferric nitrate (nonahydrate) was partially dehydrated by a modification of the above method and was used in this imperfect state of dehydration.

Guntz also prepared anhydrous manganous nitrate by treating the hydrate with nitric anhydride. As this method is too involved to be practical, it was decided to prepare the iodide, even though the halides are generally undesirable in that they are poisons for the carbon monoxide oxidation. Manganous iodide, $MnI_2 \cdot 4H_2O$, was prepared by bubbling hydrogen iodide through a mixture of manganous carbonate and water. A concentrated solution of manganous iodide was thus prepared and, when dried in vacuum, it readily yielded the anhydrous iodide (7) as a pale brownish-pink solid.

TABLE 2

Oxides prepared by slow oxidation of metals obtained by reduction in ammonia

METAL	NATURE OF PRECIPITATE IN AMMONIA	TIME OXIDE WAS WASHED	FINAL PRODUCT
		hours	
Nickel	Brownish-black	24	Black
Cobalt	Very fine black	48	Black
Iron	Black	48	Red-brown
Manganese	Grey-brown	60	Grey-brown
Copper	Bronze	60	Brownish-black

An unsilvered 300-cc. Dewar flask was used as the reaction chamber. The use of such a vessel prevented the ammonia from evaporating rapidly and allowed the outer surface of the vessel to remain unfrosted so that the reaction could be observed.

The usual procedure for the reduction was as follows: the anhydrous salt was dissolved in ammonia, and sodium, freshly cut under petroleum ether, was added piece by piece as long as any reaction took place. This method was satisfactory for nickel, cobalt, manganese, and copper.

If the above routine was followed, the reduction of the incompletely dehydrated ferric nitrate was complicated by the formation of a complex and by the tendency of the added sodium to explode. In view of these difficulties, the roughly calculated amount of sodium was added first and the ferric nitrate later. The reduction then proceeded smoothly.

The precipitated metals were in all cases separated from the ammonia by suction filtering. The suction flask had to be immersed in an ether–dry ice mush to prevent the ammonia from boiling during the filtration. The precipitate was washed on the filter by approximately one half liter of liquid ammonia. At no time was the precipitate sucked dry from ammonia; and, while the metal was still moist, it was removed from the filter and placed in a vessel such as an Erlenmeyer flask, into which air could enter only by diffusion. Although the metals all became hot enough to glow when the ammonia was removed rapidly (as was the case when the suction filtering was continued too long), the method of gradually admitting air as the ammonia slowly evaporated served as an efficient means of slow oxidation. Several hours usually suffice for the oxidation.

Manganese was so active that it became warm in the Erlenmeyer while still moist with ammonia. A cork placed loosely in the mouth of the flask cut down the supply of air sufficiently so that rapid oxidation ceased.

The metal oxides, along with sodium oxide, hydroxide, and amide as impurities, were then placed on the suction filter and washed with water. The purification was continued until the water in the suction flask failed to give any test for sodium. The oxides (see table 2) were then dried and tested for catalytic effect.

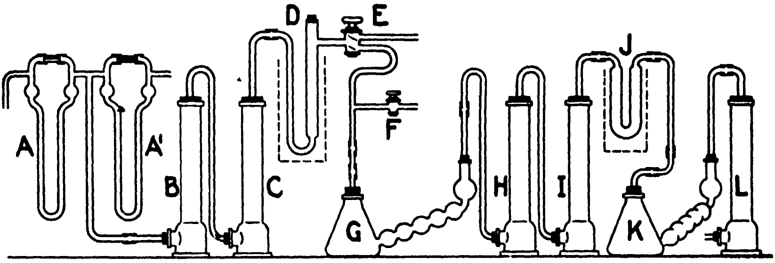

FIG. 1. CARBON MONOXIDE OXIDATION TRAIN

The results of the above procedures are given in table 2.

METHOD OF TESTING CATALYTIC EFFICIENCIES

The apparatus for testing the efficiency of the catalyst is shown in figure 1. Two flowmeters, A and A′, controlled the rate of the flow of carbon monoxide and oxygen. The valves of the carbon monoxide and oxygen storage tanks were adjusted to give a 1 per cent mixture of carbon monoxide in oxygen at a rate of 100 cc. per minute. The gases passed through a soda-lime tower, B, and a phosphorus pentoxide tower, C. The gaseous mixture then passed through the U-tube, D, which contained a 1 sq. cm. x 10 cm. bed of the catalyst. The carbon dioxide, formed during the passage over the catalyst, was absorbed in a solution of barium hydroxide contained in G. The residual gases were then swept through the soda-lime tower, H, and the phosphorus pentoxide tower, I. The dry mixture then passed through the U-tube, J, containing hopcalite maintained at 150°C. Any carbon monoxide which remained in the gas was completely oxidized by the hopcalite and was absorbed by the barium hydroxide in K. The remaining gas passed out through the soda-lime tower, L.

Stopcocks E and F were convenient for sweeping out the system and for regulating pressure when introducing barium hydroxide into the bubble tubes.

The catalysts obtained as hard lumps were broken up into smaller granules and sealed into the U-tube. Others of the oxides, in the form of fine powder, were packed in the tube with pieces of broken glass so as to decrease the resistance to the gas stream. The tube containing the catalyst was placed in the train and heated to 150–200°C. while a current of oxygen passed through the system. This treatment, continued for several hours, served at once to dry the catalyst, to further the oxidation of any of the metal that had not been oxidized at room temperatures, and to remove any carbon dioxide from the train. Fifty cubic centimeters of a standard solution of barium hydroxide was introduced into each bubble tube, and the flow of the gases through the system started. After running

TABLE 3

Efficiencies of the catalysts expressed in per cent

TEMPERATURES	−78°C	−40°C	0°C	30°C	100°C	150°C
Oxides prepared by distillation of mercury and activation in oxygen						
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Nickel				6	49	90
Cobalt	80	100				
Iron				7	50	100
Manganese*				5	38	62
Copper				2	24	
Oxides of metals prepared by reduction in ammonia						
Nickel				24	72	100
Cobalt†	100					
Iron					40	100
Manganese		0	100			
Copper				52	100	100

* Manganese and cobalt oxides, prepared by direct oxidation of the amalgam, were even more active, the latter being 100 per cent efficient at −78°C.

† The cobalt oxide was also tested before washing, when it contained at least 10 per cent impurity. Even with this large amount of sodium present, the oxide was 100 per cent efficient at 0°C All the carbon dioxide formed by the oxidation was taken up by the sodium oxide, no carbon dioxide showing up in either bubble tube.

the test for the desired length of time, usually twenty minutes, the efficiency of the catalyst (see table 3) could be obtained by a determination of the amounts of barium hydroxide used up in the two bubble tubes. The percentage efficiency is the amount of barium hydroxide used up in the first bubble tube divided by the amount used in both bubble tubes. This was determined by titrating the unchanged barium hydroxide with standard acid.

COMPOSITION OF THE CATALYSTS

The catalysts from the amalgams were examined for mercury by precipitating with hydrogen sulfide. The cobalt and nickel catalysts showed the presence of a trace of mercury, but in the case of the other metals no mercury was found. It is unlikely that the small amount of mercury present would have any effect on the reaction.

In the case of the catalysts prepared by oxidation of metals precipitated in ammonia, sodium must have been present in small amounts. However, alkalies have been shown to be poisons for this reaction (8) and could certainly have exerted no promoter action.

TABLE 4

Comparison of activities of oxides

METALS	PRECIPITATED OXIDES (BENNETT)		OXIDES FROM AMALGAMS		OXIDES OF METALS FROM AMMONIA	
	At 30°C	At 100°C	At 30°C	At 100°C	At 30°C	At 100°C
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Nickel	100	100	6	49	24	72
Cobalt	100	100	100	100	100	100
Iron	0	1	7	50		40
Manganese	100	100	5	38	100	100
Copper	Reduction	100	2	24	52	100

The amount of oxygen in the catalyst had no meaning. For example, analysis of one of the cobalt catalysts showed slightly less oxygen than corresponded to 2 oxygen:3 cobalt. In all cases the amount of oxygen varied according to the conditions of activation.

As is evident, it was not attempted to obtain a catalyst of definite composition, but it *was* shown here that the active metallic surface may be changed into an active oxide surface by a process of low temperature oxidation.

RELATIVE EFFICIENCIES OF OXIDIZED METALS AS CATALYSTS

Some idea of the activities of these oxides relative to those of precipitated oxides may be obtained from table 4.

As is evident from table 4, the method developed in this paper does not give oxides any more active than those precipitated and carefully purified. It does, however, offer another general method of preparing oxides whose activity is certainly comparable to that of those prepared by precipitation.

The percentage efficiencies given for the oxidized metals may be made to parallel those for the precipitated oxides even more closely if the following facts are taken into account.

The low results for nickel and manganese oxides from the amalgams are due to the insufficient oxidation of the metal. The oxides can be made more efficient by longer heating in oxygen.

Higher efficiencies may be expected in the case of nickel and manganese oxides (prepared by reduction in ammonia) if the washing is continued longer. The results given in table 4 are for the oxide washed for only one or two days. Longer purification slowly increased the efficiency.

The efficiencies of oxidized iron and copper are listed higher than those of the precipitated oxides. The results given in this work, however, are for a twenty minute run. At least part of the carbon monoxide oxidation below 100°C. involves chemical reduction of the oxides, for subsequent runs show decreasing efficiency of the catalyst.

The results obtained in this present work bring out an interesting point. It is the general belief that manganese dioxide is more active catalytically than the other oxides and that its presence as the essential oxide in commercial catalysts is uniquely responsible for the efficiency of those catalysts. The data presented here seemed to show that the oxide of cobalt is more active, or, at least, that it is less sensitive to impurities and generally easier to prepare in an active form.

SUMMARY

1. Methods have been developed for the low temperature oxidation of pyrophoric metals.

2. The oxidized metals have been tested as catalysts for the carbon monoxide oxidation. They have been found to be comparable in activity to the most carefully purified precipitated oxides.

REFERENCES

(1) Whitesell and Frazer: J. Am. Chem. Soc. **45**, 2481 (1923).
(2) Williams: Dissertation, The Johns Hopkins University, 1928.
(3) Bennett: Dissertation, The Johns Hopkins University, 1930.
(4) Feree: Compt. rend. **121**, 822 (1895).
(5) Burgess: Chem. Rev. **8**, 271 (1931).
(6) Guntz and Martin: Bull. soc. chim. **5**, 1004 (1909).
(7) Peters, W.: Ber. **42**, 4826 (1909).
(8) Bennett: Dissertation, The Johns Hopkins University, 1930.

THE PHYSICAL CHEMISTRY OF FLOTATION. I

THE SIGNIFICANCE OF CONTACT ANGLE IN FLOTATION

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INTRODUCTION

Adhesion between a bubble of air and a solid surface is the basis of the flotation process. In order that a small particle of mineral may become incorporated in the froth at the top of the machine, it is necessary first for it to become attached to (i.e., to adhere to) an air bubble of sufficient buoyancy to carry it upwards. It is the purpose of this communication to investigate some of the physical and chemical principles underlying the adhesion between a bubble of air and a single solid particle and to draw attention to some of the problems awaiting solution before an explanation of the physical nature and behavior of froth systems can be obtained. The froth differs from the simple case in which a single particle is considered, in that each bubble is coated by numerous small particles of mineral instead of merely being attached to one particle. Nevertheless a discussion of the principles involved for a single particle may be of some value in considering the general case.

It has been shown (1) in the course of an investigation being carried out in the University of Melbourne for and at the expense of a group of mining companies[1] that an air bubble in water will not adhere to a clean surface of any of the common sulfide or gangue minerals or to metals. When, however, a unimolecular film of a xanthate is adsorbed by the mineral, the air of the bubble spreads to a limited extent over the mineral surface, partly replacing the aqueous phase in so doing. Spreading continues until a definite angle between the air–water interface and the water–mineral interface, θ, is attained which is determined by the well-known relationship:-

$$\cos\theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

where T_{as}, T_{sw}, and T_{wa} are the surface tensions at the air–solid, solid–water, and water–air interfaces, respectively. Different conditions of the mineral surface and different reagents lead to variations in the contact angle. One of the major objects of this paper is to investigate the significance of changing contact angle on the tenacity of contact between air and mineral and, through it, on floatability. Incidentally, it should be noted that the molecular mechanism through which adhesion is achieved is unimportant in thermodynamical and mechanical discussions.

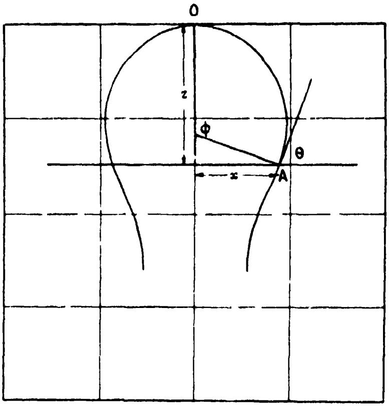

FIG. 1

I. EQUATION TO THE SURFACE OF A STATIONARY BUBBLE OF AIR IN WATER

All theories of capillarity are in agreement concerning the difference in pressure on the two sides of a curved interface between two fluids, namely, that this pressure difference at any point is equal to

$$_{wa}\left(\frac{1}{R} + \frac{1}{R'}\right)$$

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[1] Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Co. of A/asia Ltd., Mt. Lyell Mining and Railway Co., Burma Corporation Ltd.

where T_{wa} is the surface tension and R and R' are the two principal radii of curvature at that point. Assuming this difference in pressure, Bashforth and Adams (2) show how the equation to the surface may be derived. Since this work is not generally available, a modified development is presented here. Let P_O and P_O' be the pressures on the inner and outer sides, respectively, of the surface at O and P_A and P_A' be the corresponding pressures at any point A. Let ϕ be the angle which the normal to the surface at A makes with the axis of revolution, and let θ be its supplement. The two principal radii of curvature are equal at O; let each be denoted by b. One of the two principal radii of curvature at A is $x/\sin\phi$; let the other be denoted by ρ. It is obvious that

$$P_A - P_O = \sigma_1 g z \tag{1}$$

and

$$P_A' - P_O' = \sigma_2 g z \tag{2}$$

where σ_1 and σ_2 are the densities of air and water respectively. Then

$$P_O - P_O' = T_{wa} \cdot 2/b \tag{3}$$

$$P_A - P_A' = T_{wa}\left(\frac{\sin\phi}{x} + \frac{1}{\rho}\right) \tag{4}$$

Whence, subtracting equations 3 and 4 and substituting from equations 1 and 2,

$$gz\ (\sigma_1 - \sigma_2) = T_{wa}\left(\frac{\sin\phi}{x} + \frac{1}{\rho} - \frac{2}{b}\right) \tag{5}$$

or

$$\frac{2}{b} + \frac{gz\ (\sigma_1 - \sigma_2)}{T_{wa}} = \frac{\sin\phi}{x} + \frac{1}{\rho} \tag{6}$$

In the case of a bubble of air in a liquid, $\sigma_1 - \sigma_2$ is negative.

Following Bashforth and Adams let

$$\frac{gb^2\ (\sigma_1 - \sigma_2)}{T_{wa}} = \beta$$

Equation 6 then becomes

$$\frac{1}{\rho} + \frac{\sin\phi}{x} = \frac{2}{b} + \frac{\beta z}{b^2} \tag{7}$$

in which β is negative.

If ρ and ϕ are expressed[2] in terms of x and z it becomes apparent that the differential equation cannot be exactly solved. Using equation 6, Bashforth and Adams have constructed tables by which corresponding values

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[2] Expression of ρ and ϕ in terms of x and z:

$$\frac{1}{\rho} = \frac{d^2z}{dx^2} \div \left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{3/2}$$

$$\sin\phi \quad \frac{dz}{dx} \div \left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{1/2}$$

of x, ϕ, and z may be approximately obtained for any given values of b and β. β determines the form of the bubble and b its magnitude, but since β depends partly on b, the magnitude of the bubble partly determines its form. These tables are extensive enough for the calculation of the shape of the interface between two fluids for which $\sigma_2 > \sigma_1$, i.e., where β is positive. Where β is negative, however, they are not nearly as comprehensive, and for bubbles of air in water it is only over a limited range that the calculations are possible.

It will be apparent that the nature of any solid surface to which the bubble of air may be attached has no influence on the shape of the bubble, for the nature of the solid cannot affect any of the pressure terms used in deriving the equation to the surface. The bubble fits on to the surface of the solid with a definite angle of contact, and above the plane of contact the shape is the same as that of a bubble of greater depth. Fortunately Bashforth and Adams tabulate the angle ϕ, which is he supplement of the angle of contact, θ, measured across the water, at the line of triple contact. This angle was directly measured in the paper already cited (1).

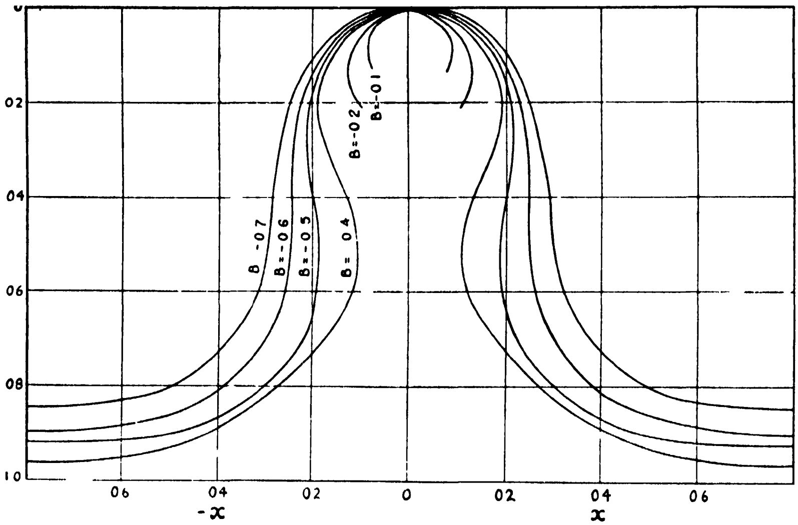

FIG. 2. SHAPES AND SIZES OF STATIONARY AIR BUBBLES IN WATER (IN CM.)

II. ARITHMETICAL SOLUTION OF THE EQUATION FOR BUBBLES OF DIFFERENT SIZES

Since

$$\beta = g \, ^{(\sigma_1 - \sigma_2)} \cdot b^2$$

and, from Kaye and Laby's Physical and Chemical Constants, $g = 980$ cm. per sec.^{2} for Melbourne, $(\sigma_1 - \sigma_2) = 0.997$ at 20°C., allowing for the saturation of the air by water vapor, and $T_{wa} = 72.8$ dynes per centimeter (Bohr's value), the value of β reduces to $-$ 13.43 b^2.

Figure 2 shows not only the shapes but the actual sizes in centimeters of a series of bubbles of air in water corresponding to different values of β. These have been calculated from Bashforth and Adams' values of x/b and z/b, and the value of b corresponding to each value of β. There is good agreement between the shapes of calculated curves and photographs of actual bubbles.

Worthington (3) states that pendant drops of liquids are unstable with regard to surface oscillations at points where they are reëntrant. The writer has not been able to obtain any reasonably stable reëntrant surfaces, though if the buoyancy of the bubble is balanced by an upper supporting tube, reëntrant surface may persist for some time in the absence of vibrations.

III. EQUATION CONNECTING VOLUME OF BUBBLE, ANGLE OF CONTACT, AND AREA OF AIR–SOLID CONTACT

Bashforth and Adams develop by two methods a formula for the volume contained by a bubble above any given plane in the bubble. The following analysis is based upon their second derivation. Assume that a mass of water of the same size and shape as that portion of the bubble being considered replaces it in the water. The vertical forces acting on this mass of water, which obviously is in equilibrium, are:

(1) Its weight $V \cdot \sigma_2 \cdot g$ acting downwards.

(2) The force due to the hydrostatic pressure P_A' at the base of the volume, $P_A' \cdot \pi \cdot x^2$ upwards.

(3) The resultant, F, (acting downwards) of the hydrostatic pressure over the curved part of the surface.

Whence

$$F + V\sigma_2 g = \pi x^2 P_A' \tag{8}$$

For the bubble of air, the vertical forces acting on the portion under consideration are:

(1) The same force, F, acting downwards.

(2) Its weight $V\sigma_1 g$ acting downwards.

(3) The surface tension force, $2\pi x T_{wa} \cdot \sin\phi$, acting downwards.

(4) The pressure of the air lying under the plane considered, $\pi x^2 P_A$. (If the bubble is cut off, not by an imaginary plane but by a solid surface, this pressure term is placed by an equal reaction acting upwards.)

Whence

$$F + V\sigma_1 g + 2\pi x T_{wa} \sin \phi = \pi x^2 P_A \tag{9}$$

Equations 8, 9, and 4 reduce to the equation of Bashforth and Adams, viz.,

$$V = \frac{\pi x^2 T_{\mathrm{wa}}}{g(\sigma_1 - \sigma_2)} \cdot \left(\frac{1}{\rho} - \frac{\sin \phi}{x}\right) \tag{10}$$

or, introducing β,

$$V = \frac{\pi b^2 x^2}{\beta} \cdot \left(\frac{1}{\rho} - \frac{\sin \phi}{x}\right) \tag{11}$$

where, as before, β is negative. Since V is always positive, $\sin \phi/x$ must always be greater than $1/\rho$. Bashforth and Adams have constructed numerical tables for different values of β and b which enable a numerical solution for V—correct, if necessary, to 1 part in 100,000—to be made over a limited range.

It would be possible to construct a three-dimensional model to show corresponding values of the three variables, V, θ, and x for any two fluids, assuming T_{wa}, $\sigma_1 - \sigma_2$, and g to be known, i.e., b^2/β to be fixed. It is, however, easier in the first place to construct sectional diagrams which represent the relationship between any two of the three variables when the third is constant. These sectional diagrams are now considered.

IV. ARITHMETICAL SOLUTION OF THE EQUATION OF III

(*a*) *θ constant.* Figure 3 shows the relationship between V and x for a series of different (constant) values of θ. The irregular choice of angles in constructing this figure was necessitated by the incompleteness of the tables upon which the calculations were based.

The meaning of the graph is best illustrated by considering for one of the curves (for example that for 90°) the shapes of the bubbles corresponding to a number of points on the curve. The numbers 3, 4, etc., correspond to those portions of the bubbles of figure 2 above $\theta = 90°$ for values of β of $-$ 0.3, 0.4 etc., respectively. The points marked 4a and 4b correspond to bubbles, one of which (4b) is merely a continuation of the other to a position where, for the second time, an angle of 90° develops. As explained above, this involves a reëntrant surface and thus for flotation the portion of the curve beyond 6a is probably unimportant.

Two important curves follow from figure 3. These show respectively (1) maximum volume of bubble for a given value of θ (figure 4) and (2) maximum value of x for given values of θ (figure 5).

The figures of figure 5 are immediately applicable in flotation, but the maximum values of V given in figure 4 all correspond to bubbles with reëntrant surfaces. The maximum values for non-reëntrant bubbles are also plotted in the dotted curve; these would be of more interest with regard to flotation.

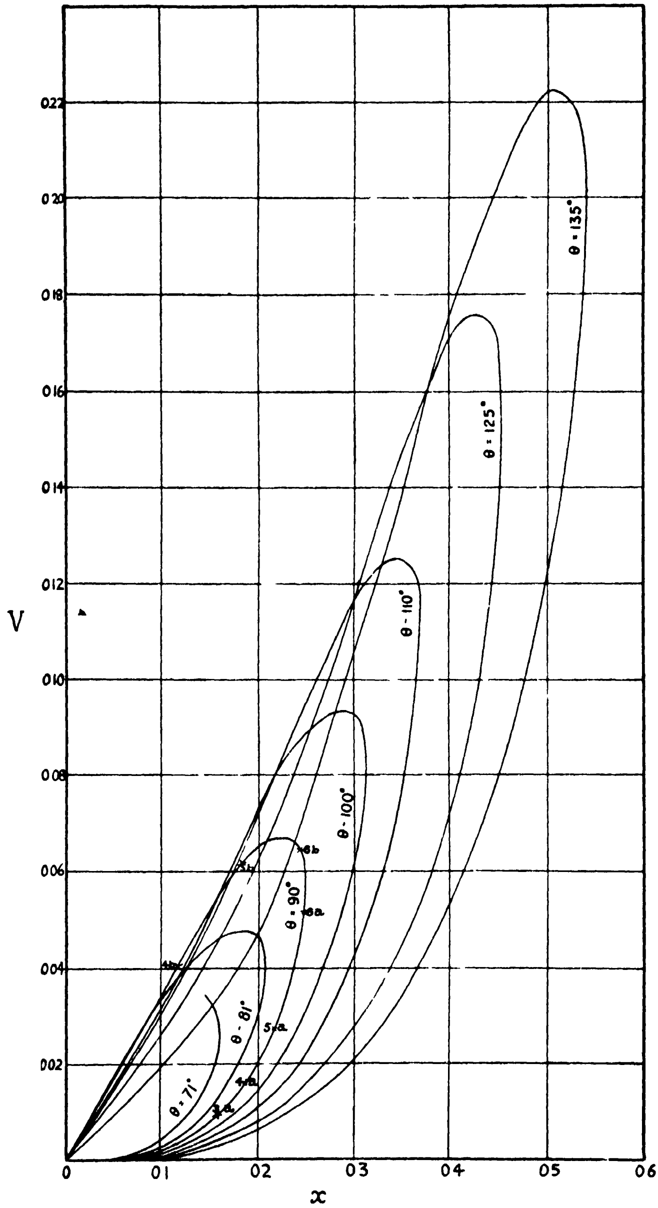

Fig. 3. Relationship Between Volume of Bubble and Radius of Circle of Contact for Various Angles of Contact

Experimental verification. Figure 5 has been verified experimentally, the points marked by a circle being experimental values. This verification

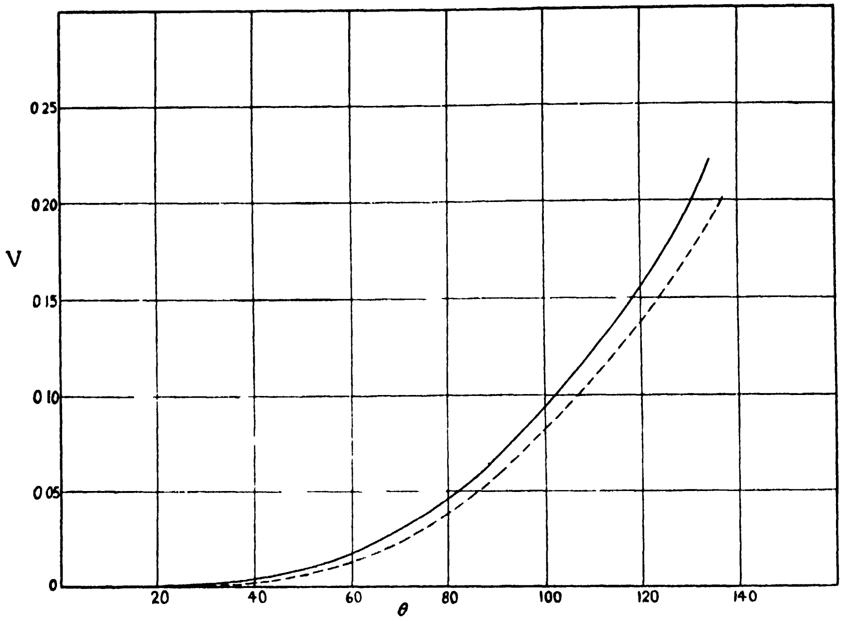

FIG. 4. MAXIMUM BUBBLE VOLUMES FOR GIVEN CONTACT ANGLES

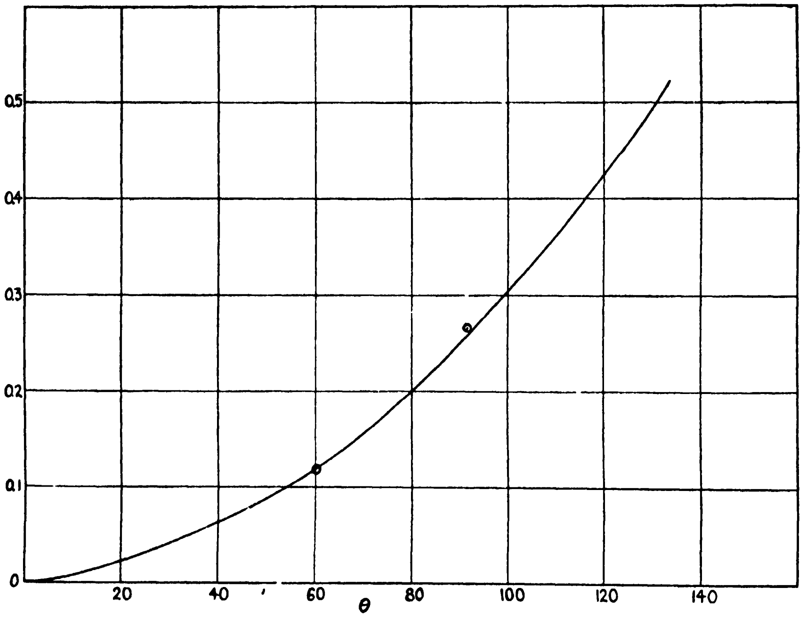

FIG. 5. MAXIMUM VALUES OF RADIUS OF CIRCLE OF CONTACT FOR GIVEN CONTACT ANGLES

⊙ Experimental points

is tedious, a large number of bubbles which will just hang to the surface being measured for a series of different xanthates, which give characteristic contact angles. The experimental points were determined by Mr. A. B. Cox without preknowledge of the position of the theoretical curve.

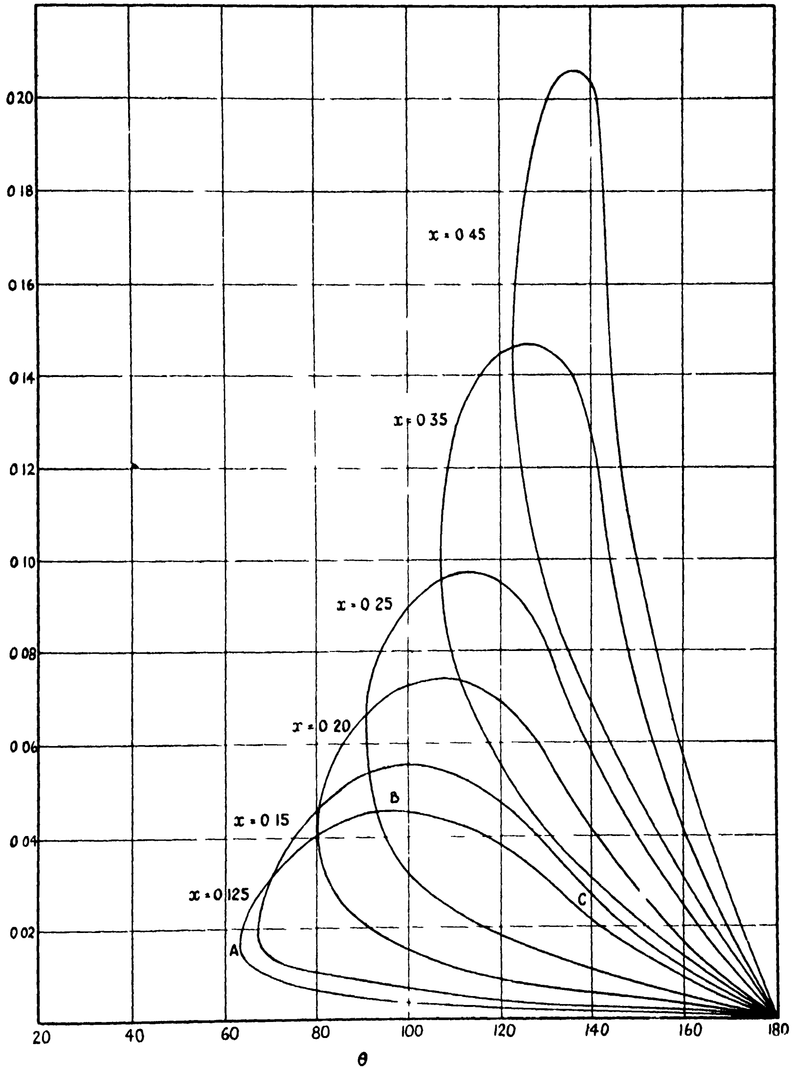

FIG. 6. RELATIONSHIP BETWEEN VOLUME OF BUBBLE AND ANGLE OF CONTACT FOR VARIOUS VALUES OF RADIUS OF CIRCLE OF CONTACT

(*b*) *x constant.* Figure 6 shows the relationship between V and θ for a series of different (constant) values of x. The meaning of the curves is

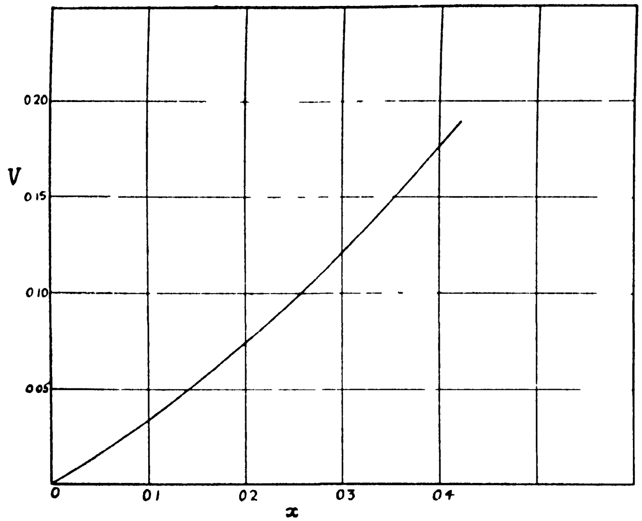

FIG. 7. MAXIMUM BUBBLE VOLUMES FOR GIVEN VALUES OF RADIUS OF CIRCLE OF CONTACT

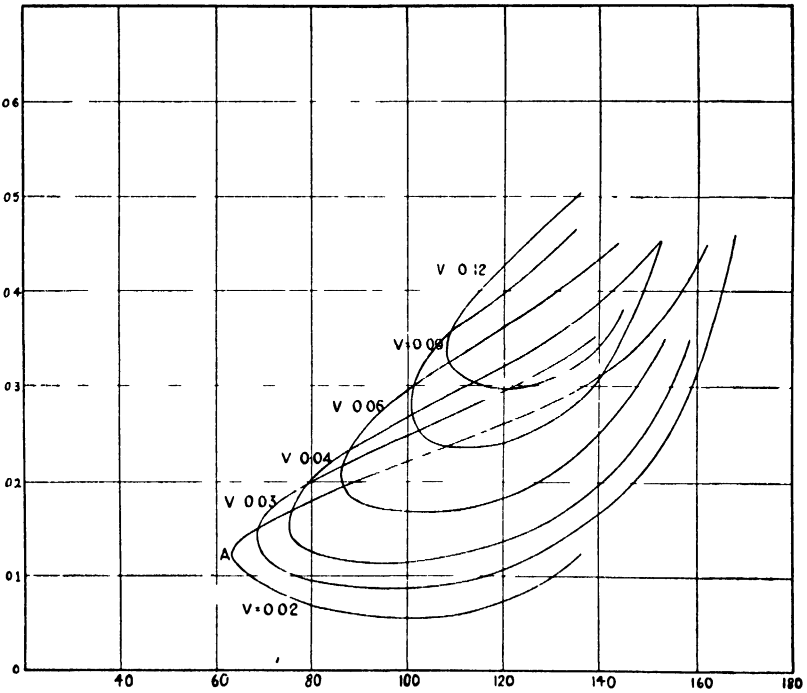

FIG. 8. RELATIONSHIP BETWEEN RADIUS OF CIRCLE OF CONTACT AND ANGLE OF CONTACT FOR VARIOUS VALUES OF BUBBLE VOLUME

again best understood by tracing, for one of the curves—e.g., that for $x = 0.125$ cm.—the shapes of the bubbles corresponding to various points on the curve. Along the portion *OA* the angle of contact is steadily decreasing to the minimum value, but along *AB* it increases again as reëntrant surfaces appear. From *B* to *C*, though the angle is still increasing, the volume is diminishing, owing to increasing flatness of the bubble.

Two important curves follow immediately from figure 6. These show, respectively, (1) the minimum value of θ for given values of x, and (2) the maximum value of V for given values of x (figure 7). It is obvious that the curve showing the minimum values of θ plotted against x is identical with that of figure 5, which shows the maximum value of x plotted against θ.

(*c*) *V constant.* Figure 8 shows the relationship between θ and x for a series of different (constant) values of V. It will be seen that both arms of any of these curves approach the x-axis asymptotically. The points on the lower arm all represent bubbles with reëntrant surfaces; at *A*, however, reëntrant surfaces disappear and from *A* back to the x-axis the bubbles have the simplest form.

V. REPLACEMENT OF SOLID–WATER CONTACT BY SOLID–AIR CONTACT

Tenacity of adhesion

The conditions which determine whether air will displace water at the surface of a solid follow immediately from thermodynamics. This has been realized by several writers, but others have given incorrect analyses. Restatement may be helpful. For any rearrangement of the surfaces to occur when an air bubble is brought into contact with a submerged mineral surface, it is necessary that the potential energy should decrease. Since, under the conditions of flotation practice, the air–mineral interface cannot be created without the simultaneous destruction of mineral–water and water–air interfaces, the condition for replacement of water by air is evidently[3]

$$T_{as} < T_{wa} + T_{sw}$$

and

$$W = T_{wa} + T_{sw} - T_{as} \qquad (12)$$

is the measure in ergs of the work done per unit area by the system during this rearrangement.

No satisfactory method is available for the determination of the surface tensions at the solid–liquid and solid–air interfaces, but the value of T_{wa}

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[3] It is shown in textbooks of physics that free surface energy in ergs per unit area and surface tension in dynes per unit length are numerically equal. Surface tensions may therefore be used in place of surface energies in these equations.

may be measured by a variety of methods Both T_{as} and T_{sw} may be eliminated, however, by introduction of the contact angle

When equilibrium is reached,

$$\cos\theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

and substituting for $T_{as} - T_{sw}$ in equation 12

$$W = T_{wa}\,(1 - \cos\theta) \tag{13}$$

which is the work done per unit area in forming the contact between air and solid (free energy of formation) at the expense of the solid–water and water–air contacts, or alternatively is the work[4] which must be expended in destroying the air–solid contact. It may thus be regarded as a measure of the tenacity of adhesion. When $\theta = 0$, the expression reduces to zero and there is no tendency for sticking; when $\theta = 180°$, the expression reaches a maximum of $2T_{wa}$. The adhesive tendency may conceivably be greater than corresponds to complete wetting by air, if $T_{as} - T_{sw} > T_{wa}$ (4), but no such cases are known.

VI. TRUE AND APPARENT AREA OF CONTACT

When a submerged bubble of air is pressed against a solid surface it sometimes fails to spread uniformly. Portions of the surface are in true contact with the air, but others may be fouled or for some other reason the air makes no true contact with them. The area of true contact will not then be identical with the apparent area of contact, and in estimating the tenacity of contact from the equation, $W = T_{wa}\,(1 - \cos\theta)$ ergs per unit area, the true rather than the apparent area of contact must be employed.

It is important that the relationship between these two areas should be known. Some experiments at a cerussite surface using a bubble of carbon tetrachloride throw light on this question. If the surface be freshly prepared in the manner described in the third paper of this series, the carbon tetrachloride does not spread immediately over the whole surface. Contact first occurs at a series of small isolated areas whose extent gradually increases. The water is gradually forced out between them and ultimately, save for a few irregular patches, there is a complete disc of contact between the carbon tetrachloride and the mineral. A few patches of the surface remain wetted by thin layers of water. These observations, which extend over only a fraction of a minute, are possible because of the high refractive index of the carbon tetrachloride. The line of vision should be at right angles to an illuminating beam of light and inclined at 20° to the horizontal.

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[4] Since the surface of the bubble is curved at the point of contact, and since, further, there is a rearrangement of the air–water interface after disruption, small corrections are necessary. The curvature introduces a "pressure" correction; that it is neligible for fairly large bubbles is proved by the absence of variation in contact angle with size of air bubble, and also follows from Lyons' work on floating lenses (J. Chem. Soc. 1930, 623).

If, however, the surface of the mineral is oiled, or is coated by what is called in flotation an organic collecting agent, the carbon tetrachloride spreads outwards very quickly, and no surface inclusions of the aqueous phase remain. It may be concluded that where the surface is in a receptive condition for air-contact, the true and apparent areas of contact are identical. This conclusion is supported by the uniform manner in which a bubble of air leaves the surface if it is pulled away.

Ostwald (5) has formulated an ingenious theory in which he claims that only a unimolecular ring of the organic collecting agent is necessary to ensure attachment of the bubble to the particle. His main evidence in favor of this theory is the very doubtful statement that sufficient collector is not present to form a unimolecular film over the whole surface. The above expression for the tenacity of sticking proves, however, that such a ring contact would be so unstable as to collapse with the slightest displacement unless the moving air–water–mineral boundary carried with it the ring of collector, i.e., that the attraction between mineral and collector was so small as to permit free movement of collector molecules over the surface. This it is not, for if a mineral which has had contact with a xanthate solution for a minute be removed and washed in several changes of water, it still retains over its whole surface the power of attachment to an air bubble. Recent measurements of surface tension (6) indicate moreover that there is little adsorption of xanthate in the air–water interface.

A contaminated patch in the center of the air–mineral contact will not, of course, influence the stability of the contact for small displacements, but it will cause a rapid unopposed contraction of the area of contact the moment the displacement of the bubble wall reaches it.

In the experiments described in the paper of Wark and Cox (1) and in those of the following papers, there has been little or no fouling of the surface. When one is approaching a region of non-sticking, however, as for example when alkali is added to a xanthate solution in contact with galena, the surface does change in such a way that the true area of contact is apparently greatly diminished. Even on a partly fouled surface, at points where sticking is possible, the full angle of contact may be developed.

VII. DIFFICULTIES IN THE EXPERIMENTAL DETERMINATION OF ANGLE OF CONTACT—HYSTERESIS

Sulman (7), Ablett (8), and Langmuir (9) have shown that the angle of contact varies according to whether the line of contact between air, water, and solid is advancing or receding. The angle θ'' is greater when the *water–solid contact is being replaced by an air–solid contact than the angle θ' when the reverse is occurring. The difference $\theta''-\theta'$ is termed the* "hysteresis."

Sulman has shown that the variation lies within certain well-defined limits, which he claimed were dependent on the mineral. Ablett also showed that the limits were clearly defined on a paraffin surface and, furthermore, that the mean of θ'' and θ' was very close to the equilibrium value, θ; also that the difference between θ'' and θ' was a function of the rate of motion, and was constant over a range from 0.4 to 4 mm. per second.

The angle of contact of a bubble in equilibrium on a solid surface is (subject to certain minor corrections) given by the expression

$$\cos \theta = \frac{T_{as} - T_{sw}}{T}$$

Edser (10) concludes that if, owing to hysteresis, θ alters, T_{as} must have altered. (It is not stated why T_{as} and not T_{sw} has been assumed to alter.) This would be true if the bubble were still in equilibrium, but under such conditions it is not. If the vessel in which the mineral rests is shaken lightly, e.g., by tapping the table upon which it stands, the angle of contact reverts to the equilibrium value θ. Hundreds of tests have supported this contention. Apart from any experimental verification, however, it is obvious that the stress applied at a point of the bubble can have no effect on the surface energies of the distant interfaces mineral–water and mineral–air.

Some secondary force must assist in the maintenance of apparent equilibrium, if variations in T_{as}, T_{sw}, etc., are inadmissable. A frictional force alone could be responsible. To make the argument specific, let it be assumed that the stress at the base has been caused by an upward extension of the bubble which has the effect of narrowing it along its length.

When the top of the bubble is raised, an attempt is made to increase the volume of the bubble. This reduces the pressure of the bubble, and thereby creates an excess external pressure which tends to push in the bubble wall. Yet some force, resulting in the hysteresis, prevents the base of the bubble from contracting, though in equalizing the pressure the bubble wall alters in shape and a new angle of contact develops. Only a horizontal opposing force could be effective in preventing motion along the mineral surface under the stress of this pressure. This horizontal force is thus responsible for the new value of the angle. Furthermore this force must disappear when true equilibrium is reëstablished, for the original angle is again obtained. Such a force, which acts parallel to the direction of possible motion and disappears when stable equilibrium is reached, is customarily styled a frictional force. Hysteresis of contact angle is thus a manifestation of friction.[5]

Adam and Jessop (11) have already suggested that hysteresis is due to friction, but their paper has not received the attention it deserves. This is perhaps due to the fact that, beyond the statement that the degree of hysteresis is less at smooth than at rough surfaces, they give no reason for this interpretation.

Our experience confirms this statement. It is by no means certain that the laws of friction at solid surfaces may be applied when considering solid–fluid contacts, but, assuming that they may, it follows that the frictional force opposing motion of the bubble over the surface is proportional to our L of equation 16.

Assuming that hysteresis is due to friction, Adams and Jessop develop a formula for θ, namely,

$$\cos\theta = 1/2\,(\cos\theta'' + \cos\theta') \tag{14}$$

In deriving this expression the authors equate terms of unequal dimensions, but their final expression is correct. If H dynes per centimeter of air–water–mineral boundary be the frictional force it may be shown that

$$H = 1/2\,T_{\mathrm{wa}}\,(\cos\theta' - \cos\theta'') \tag{15}$$

Since $\theta'' - \theta'$ may be as high as 60°, the frictional force may be of an order of magnitude as high as one-quarter that of the surface tension.

Ablett's results for paraffin wax are accurate enough for testing equation 14. He found that

$$\theta'' = 113°9'$$

and

$$\theta' = 96°20'$$

Whence

$$1/2\,(\cos\theta'' + \cos\theta') = 0.2517$$

and

$$\theta_{\mathrm{calc}} = 104°35'$$

Ablett's θ, as measured, was 104°34′. Ablett wrongly expected $1/2\,(\theta'' + \theta')$ to equal θ. The mean value is 104°44′ which differs from the determined value of θ by more than the experimental error. A better check of the theory could be obtained when using smaller values of θ, for which the difference between mean and cosine mean is greater.

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[5] The difference between interfacial energy (or tension) and friction is as follows: Interfacial energy changes become manifest with destruction and creation of interfaces; the frictional force and energy consumed thereby are associated with displacements of surfaces, not primarily with changes in their extent.

VIII. THE STABILITY OF AIR–MINERAL ATTACHMENTS

There has been some misconception with regard to the influence of hysteresis on the stability of air–mineral aggregates. Though there may be some justification for Sulman's claim that hysteresis imparts a greater range of stability to a floated particle, there can be none for Edser's statement that, "No particle could float stably but for the possibility of variation of the contact angle, for if this were constant, a slight tilt would inevitably cause the particle to sink." Sulman later (b) states, "But for hysteresis a mineralized bubble could only have a brief existence." Were these statements correct the measurement of contact angle would lose some of the significance which we have given to it. It would need to be supported by an estimation of the hysteresis. It devolves upon us, therefore, to explain why it is considered that these statements are incorrect.

It has been proved above that when the air–mineral contact is formed there is a decrease in free energy of the system amounting to $T\ (1 - \cos\theta)$ ergs per cm.^{2} of contact. Since $(1 - \cos\theta)$ is always positive, there is invariably a *decrease* of free energy on the sticking of the bubble. This amounts to saying that the process occurs spontaneously. To liberate the air bubble from the surface would require the expenditure of an equal amount of work. This implies that the equilibrium is a stable one with regard to attempts at disruption.

While contact between mineral and air is being established, and the air is spreading over the surface of the mineral from a small nuclear point of attachment, frictional forces would tend to retard the spreading. There would thus be a tendency to prevent the true equilibrium angle and area of contact being reached, so that the maximum tenacity of sticking between air and mineral would develop rather slowly. Nevertheless, because of the violent agitation in the flotation boxes, it is probable that the true contact angle would develop within a reasonable time. The initial effect of hysteresis is therefore to prevent maximum attachment between air and mineral, which is the primary step in flotation.

The effects of hysteresis on the stability of an attachment already established must also be considered. It is obvious that, as the contact angle can be raised slightly by hysteresis, the stability of contact under a transient stress can be increased—momentarily at least. Sulman's claim that hysteresis imparts a greater range of stability is thus justified in this case.

An analysis of the effects of all possible types of stress which may be applied to a bubble in contact with a mineral surface leaves one in doubt whether hysteresis ever imparts much greater stability to the attachment.

The bubble and mineral must part company by relative motion in a direction at right angles to the surface and the force of friction, being parallel to the surface, cannot be effective in preventing such motion. On the other hand, friction does oppose easy motion of a bubble over the surface of a solid or of a solid over the surface of a bubble, but this is probably disadvantageous.

Some experiments with diphenyl ether $C_6H_5OC_6H_5$ confirm these views. The density of this substance is 1.07 and it melts at 28°C. If the melt be allowed to cool on a glass plate, very large smooth crystals form. On the smooth surface there is practically no hysteresis effect, yet nothing known to us floats so readily. It is true that the floatability of large plates of the compound by very small bubbles is due to the very small difference between its density and that of water, but the ability of the aggregate to withstand large stresses is, we suspect, due to the absence of hysteresis and the consequent flexibility which enables adjustment of the partners of the aggregate to meet any external stress.

Extension to moving systems

Even when air–mineral attachment is possible, there are certain other conditions to be fulfilled in order that a particle may float.

The capillary force of attraction between air and mineral must obviously be greater than their tendency to part. The capillary force of attraction, L, corrected for the hydrostatic pressure difference has been shown to be given by the expression,

$$L = 2\pi x T_{\mathrm{wa}} \sin\theta - \pi x^2 T_{\mathrm{wa}} \left(\frac{\sin\phi}{x} + \frac{1}{\rho}\right)$$

or, since θ is the supplement of ϕ,

$$L = \pi x T_{\mathrm{wa}} \left(\sin\theta - \frac{x}{\rho}\right)$$

The tendency to part may be evaluated from considerations of the dynamics of the motion of the air–mineral aggregate. Let the tension between mineral and air be E. Let σ_1, σ_2, and σ_3 be the densities of air, flotation liquor, and solid respectively, and let V_1 and V_2 be the volumes of air and mineral in the small aggregate under consideration. Let the acceleration of the system be f upwards.

Considering the motions of the bubble and particle separately;

$$v_1 g(\sigma_2 - \sigma_1) - E = v_1 \sigma_1 f$$

and

$$E - v_2 g(\sigma_3 - \sigma_2) = v_2 \sigma_3 f$$

Whence

$$E = g\sigma_2 v_1 v_2 \left(\frac{\sigma_3 - \sigma_1}{v_1\sigma_1 + v_2\sigma_3}\right) \tag{17}$$

and

$$f = g\left\{\frac{(v_1 + v_2)\sigma_2 - (v_1\sigma_1 + v_2\sigma_3)}{v_1\sigma_1 + v_2\sigma_3}\right\}. \tag{18}$$

If σ_1 may be neglected, $E = v_1 g\sigma_2$, which is equal to the upward thrust due to the buoyancy of the air.

Three cases arise:

(1) The bubble and mineral both sink if f is negative, that is, if

$$v_1\sigma_1 + v_2\sigma_3 > (v_1 + v_2)\sigma_2 \quad \text{and} \quad L > E$$

(2) The bubble and mineral both rise if f is positive, i.e., if

$$v_1\sigma_1 + v_2\sigma_3 < (v_1 + v_2)\sigma_2 \quad \text{and} \quad L > E$$

(3) The bubble and mineral part company if

$$L < E$$

Yet another contingency may arise. It is possible that disruption of the bubble itself may occur in preference to separation of the air–mineral contact. Let S be the area of this contact. If S_1 be the area of the bubble at the level where disruption occurs, the work done against the cohesive forces is $2S_1T_{\text{wa}}$. If

$$2S_1T_{\text{wa}} < S \cdot T_{\text{wa}}(1 - \cos\theta)$$

the bubble will therefore break in preference to separation of air and mineral. Practically, this means that the bubble should have a reëntrant surface and in general is obtained only with bubbles whose contact angle exceeds 90°. This explains why only bubbles whose contact angle is is above 90° leave a residual small bubble if they are forced by increasing size to leave the surface.

IX. FROTHS AND AIR–MINERAL AGGREGATES

Regarding the size of the air bubble as infinite, the principles of the preceding sections are directly applicable to film flotation, but film flotation is unimportant nowadays. A frothing agent is invariably added to promote the formation of a relatively stable froth. A large surface for collecting the minerals is thereby provided.

The physical principles underlying the formation of a froth have been clearly defined by Edser (10), but there is much confusion in the subsequent literature of flotation. They will be summarized here in so far as this is necessary for the development of certain deductions. For froth formation it is necessary that the soluble frother should be used in such a concentration that there is a finite (positive or negative) rate of change of surface tension with respect to concentration. Only when this condition is satisfied is there adsorption of the frother in the air–liquid interface, but the amount of adsorption is dependent on $-C \cdot \frac{dT_{wa}}{dC}$ where C is the concentration, and T_{wa} is the static surface tension. The dynamic surface tension differs less from that of pure water than does the static. Edser demonstrates that any sudden strain applied to the surface will displace the adsorption equilibrium in such a manner that the surface tension is raised; in extreme cases the dynamic value may be reached. The value of the restorative force is therefore dependent upon the difference between the static and dynamic values of the surface tension.

Certain observations which do not seem to have been recorded elsewhere, though they must surely be familiar to the operators of flotation plants, may be explained along similar lines. There is a correlation between the size of bubble in and stability of the froth and the concentration of the frother. Starting with very dilute solutions the stablest bubbles are large; as the concentration of the frother is increased, the average size of the relatively stable bubbles becomes smaller, until ultimately (12), no stable froth can be obtained when the solution becomes saturated. In the most dilute solutions there is probably insufficient adsorption of the frother at the surface to prevent coalescence between the bubbles or to exert much stabilizing influence on those that are formed; the bubbles are large and ephemeral. With more of the frother present coalescence is inhibited, for with each coalescence there is a decrease in total area of film surface and a consequent additional increase in the concentration of the frother in the new bubble. Relatively stable bubbles form and the size of these does not vary over very wide limits. Some coalescence still occurs, resulting in larger bubbles which collapse on rising to the surface. The reason for the empirical rule of Gaudin, Haynes, and Haas is not clear, but it must be connected with the appearance of a film of oil as a discrete phase.

Air–mineral aggregates

Bartsch (13) has investigated the influence of insoluble oils, of colloidal particles, of gangue and sulfide minerals and of soluble salts on the solubility of the froth produced by a soluble frother. This paper is of outstanding importance with respect to stability of froth systems. It is of an empirical nature, however, and some consideration of the theoretical basis is desirable.

Some of the conclusions of the preceding sections may be applied in the study of air–mineral aggregates. It follows, for instance, from the fundamental equation for contact angle, that the contact angles at each of the mineral particles armoring a bubble are uninfluenced by the presence of the other particles.[6] The shape of the bubble, however, would be determined by the particles.

The particles collected by a bubble on its way to the surface slide downwards until they receive lateral support from the more or less continuous film of particles at the bottom. As the bubble becomes mineralized, each particle becomes more and more nearly surrounded by others, but each particle makes contact with both air and water. When the bubble reaches the froth proper, it meets a shower of particles from collapsed bubbles sliding downwards between the bubbles, and many of these are captured. Those bubbles which become most completely covered are the most stable. If they are not collected when they reach the surface, they, too, collapse. The rate of collapse may, however, be exceedingly slow. The slow rate of collapse is probably due to prevention of rapid draining by the solid particles. At the top of the froth, much of the mineral liberated as the bubbles collapse is supported by those particles which are still securely bound to the froth. Lower down, the bubbles are separated by columns of liquid, some of which are thin, and it is at the surfaces between the water columns and the air bubbles that the particles ride. Some particles may effect contact with two neighboring bubbles of air, but whether this would increase or decrease the stability of the mineralized froth systems, it is difficult to decide.

X. MAXIMUM SIZE OF PARTICLE WHICH WILL FLOAT

Edser (10) shows that a very large particle can be floated by "skin flotation" at an air–water interface. A disc of large radius is supported almost entirely by the hydrostatic pressure of the water, "the surface tension serving merely to prevent the liquid from flowing over the disc." Such a disc must be thin, however, and Edser shows how its thickness may be calculated.

Gaudin, Groh, and Henderson (14) have attempted to calculate the maximum size of a galena particle floatable by skin flotation. They have, however, neglected the term due to hydrostatic pressure differences. They show that the surface tension forces are large enough to float a cube of galena with an edge length of 2 mm., but they do not demonstrate that sufficient water is displaced to provide sufficient buoyancy, which is of course an essential for flotation. Figure 9 of Edser's paper suggests that the buoyancy would be insufficient.

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[6] If water drains away the particle may ultimately be supported by other particles and not by capillary forces; there would be no angle of contact in such a case

If applied to flotation by a single bubble, their method is therefore equivalent to using the expression

$$V_1(\sigma_2 - \sigma_1)g = 2\pi x T_{wa} \sin \theta$$

in place of our equation 10.[7]

When $f = 0$,

$$V_1(\sigma_2 - \sigma_1) = V_2(\sigma_3 - \sigma_2)$$

and from these equations V_2 can be calculated. However, using the principles of the preceding sections, allowance can be made for the differences in hydrostatic pressure, and thus a closer approximation to maximum floatable size of particle by a submerged bubble may be obtained. It should be remembered, however, that the calculation is valid only for a particle possessing a large flat surface. This surface must be of sufficient extent for the bubble of maximum volume for a given contact angle to fit on the surface without touching the edges of the particle. The maximum volume of air for a given contact angle may then be determined from figure 3, and also the corresponding area of contact. The values apply strictly only for stationary systems, but they would also be applicable to the limiting case of a particle just so big that the bubble could carry it to the surface with an infinitesimally small acceleration. Then if σ_1 may be neglected it follows, since $f = 0$, that

$$V_1\sigma_2 = V_2(\sigma_3 - \sigma_2) \tag{19}$$

To take a specific case, let us calculate the size of the largest particle of galena which could be floated for an angle of contact of 90°. From figure 3 the maximum value of x is 0.25 cm., i.e., the diameter of the circle of contact with the bubble must be 0.5 cm. and its volume, read from figure 3, is 0.06 cm.^{3} (The bigger volumes of figure 3 correspond to bubbles with reëntrant surfaces, which are of no interest in flotation.) A bubble of this size could, by equation 19, float a particle of galena (density 7.5) of volume 0.06/(7.5 − 1) cm.^{3} i.e., 0.0092 cm.^{3} The thickness of this particle would be not greater than 0.005 cm.

For an angle of contact of 125°, the maximum value of x is 0.46 and the corresponding volume of air is 0.15 cm.^{3} This would float a particle of galena 0.023 cm.^{3} If, however, still keeping θ at 125° we again make x = 0.25, V becomes 0.015 cm.^{3} and the biggest particle which can be floated is but one-quarter the thickness that can be floated for the smaller angle of 90°. This is because the bubble corresponding to the higher angle is the flatter. It is apparent, therefore, in the special case of the flotation of a single particle by a single bubble that the higher of two possible contact angles may not lead to the best flotation. It might be wondered whether the observed low collecting power of the higher xanthates may be due, in part, to the high angles of contact produced by them, but it must be borne in mind that amyl xanthate, which is a good collector, leads to an angle of contact not far short of the maximum value for xanthates.

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[7] This approximation is similar to that formerly in use for the estimation of surface tension by the drop weight method, but now rendered unnecessary by the use of certain tables based upon the equation of Bashforth and Adams.

In practical flotation there are several other factors which influence the maximum floatable size of particle. Firstly, the air–water interface may touch the edges of the particle. The contact angle might then differ slightly from that at a plane surface and in any case it no longer determines the slope of the air–water interface with the vertical. Larger bubbles may therefore be attached for a given contact angle, and very small cubes of galena may be floated because of this factor alone. Secondly, contact with more than one face of the particle may be possible. Thirdly, when the bubble is armored by a large number of small particles, it may, for a given base of contact and a given contact angle with one particle, have a much larger volume than is possible if that particle alone were attached to it. It is impossible to evaluate mathematically the significance of these factors and therefore the maximum floatable size of particle in a flotation machine cannot be exactly evaluated. Gaudin, Groh, and Henderson state that the coarsest galena particles on which reliable flotation was obtained in machines is about 0.4 mm. diameter.

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REFERENCES

(1) Wark and Cox: Am. Inst. Mining Met. Engrs., Tech. Pub. 461.
(2) Bashforth and Adams: Capillary Action. Cambridge (1883).
(3) Worthington: Proc. Roy. Soc. London **32**, 362 (1881).
(4) Bartell and Osterhof: Colloid Symposium Monograph V, 113 (1928).
(5) Ostwald: Kolloid-Z. **58**, 179 (1932).
(6) de Will et al.: J. Am. Chem. Soc. **54**, 444, 455 (1932).
(7) Sulman: Trans. Inst. Mining Met. **29**, 44 (1919), and Third Empire Min. and Met. Congress, South Africa, 1930.
(8) Ablett: Phil. Mag. **46**, 244 (1932).
(9) Langmuir: Trans. Faraday Soc. (Pt. III) **15**, 62–74 (1920).
(10) Edser: Brit. Assocn. Repts. on Colloid Chemistry 4, 263 (1922).
(11) Adam and Jessop: J. Chem. Soc. **1925**, 1865.
(12) Gaudin, Haynes, and Haas: Flotation Fundamentals, Part 4, p. 19. University of Utah.
(13) Bartsch: Kolloidchem. Beihefte 20, 1 (1924).
(14) Gaudin, Groh, and Henderson: Am. Inst. Mining Met. Engrs., Tech. Pub. 414 (1931).

THE APPLICATION OF THE LAW OF MATHEMATICAL PROBABILITY TO THE BEHAVIOR OF GASES IN THEIR PRESSURE–VOLUME–TEMPERATURE RELATIONS[1]

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The equation,

$$y = y_{\infty} kx^K/(1 + kx^K)$$

has been shown to hold for the course of a large variety of natural processes (1), and it is of interest to find that it also applies to the behavior of a gas in its pressure–volume–temperature relations. In the present case the equation assumes the form,

$$1/V_P = kP^K/(1 + kP^K)V_{\infty} \tag{1}$$

where V_P denotes the volume at any pressure, P; V_{∞}, the ultimate molal volume of the gas; and k and K are constants, characteristic of the gas considered.

V is expressed in standard units, i.e., the volume of a mole of gas at standard conditions is taken as unity. P is expressed in atmospheres. Equation 1 may also be written in the form,

$$V_{\infty}/(V_P - V_{\infty}) = kP^K \tag{2}$$

and, at 1 atmosphere pressure may be written,

$$V_{\infty}/(V_1 - V_{\infty}) = k \tag{3}$$

Dividing equation 2 by equation 3, we obtain,

$$(V_1 - V_{\infty})/(V_P - V_{\infty}) = P^K \tag{4}$$

In testing the constancy of K in equation 4, it was assumed for convenience of calculation that at 1 atmosphere pressure Charles' Law is obeyed, i.e., $V_1 = V_0T/T_0$, where $V_0 = 1$ and $T_0 = 273°\text{A}$. V_{∞} is given by the point of inflection on the curve obtained by plotting on a rather

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[1] Read before the Mathematical Association of America, Southern California Section, San Diego Teachers College, March, 1932.

TABLE 1

Hydrogen gas

P	*T* = 0°C		*T* = 15.5°C		*T* = 99.3°C		*T* = 200.3°C	
	1/*V*	*K*	1/*V*	*K*	1/*V*	*K*	1/V	*K*
atm 1	1		0.9463		0.7334		0.5768	
100	93.5	0.999	88.6	0.998	101.6	0.998	81.2	0.999
150	136.0	0.999	129.0	0.998	132.2	0.997	106.2	0.998
200	175.7	0.999	166.9	0.998	161.3	0.997	130.2	0.998
250	213.2	0.999	202.4	0.997	189.2	0.997	153.4	0.998
300	248.1	0.998	236.5	0.997	215.7	0.997	175.6	0.997
350	280.9	0.998	268.2	0.997	241.1	0.997	197.0	0.997
400	311.8	0.997	298.3	0.997	265.5	0.997	217.8	0.997
450	340.9	0.997	326.6	0.996	288.8	0.996	237.5	0.997
500	368.6	0.996	353.4	0.996	311.1	0.996	257.0	0.996
550	394.8	0.996	378.8	0.995	332.7	0.996	275.7	0.996
600	318.9	0.995	402.9	0.995	353.2	0.995	293.9	0.996
650	442.7	0.995	426.1	0.994	373.1	0.995	311.4	0.996
700	465.1	0.994	447.9	0.994	392.0	0.995	328.4	0.996
750	487.1	0.994	469.3	0.994	410.5	0.994	344.8	0.995
800	507.6	0.994	489.0	0.993	428.1	0.994	360.8	0.995
850	532.2	0.995	509.2	0.993	445.6	0.994	376.4	0.995
900	544.9	0.992	527.5	0.993	460.0	0.993		———
950	563.8	0.993	545.8	0.993	477.8	0.993		
1000	579.7	0.992	562.8	0.993		———		
1100	610.9	0.991	593.5	0.992				
1200	642.0	0.991	623.4	0.991				
1300	670.7	0.990	652.3	0.991				
1400	698.3	0.990	679.3	0.991				
1500	724.6	0.991	705.2	0.991				
1600	749.3	0.991	729.9	0.991				
1700	772.5	0.991	754.1	0.992				
1800	794.9	0.992	776.4	0.992				
1900	816.3	0.992	797.1	0.993				
2000	837.2	0.993	818.0	0.993				
2100	857.3	0.993	837.5	0.994				
2200	876.4	0.995	855.8	0.994				
2300	894.5	0.995	873.7	0.994				
2400	911.1	0.995	887.4	0.994				
2500	927.6	0.996	908.3	0.996				
2600	948.2	0.998	923.7	0.997				
2700	959.7	0.998	940.7	0.998				
2800	975.8	0.999	956.9	1.000				
2900		———	972.8	1.001				
3000			987.6	1.002				
				———				
∞	1500.0	Av. = 0.994	1500.0	Av. = 0.995	1500.0	Av. = 0.996	1500.0	Av. = 0.997

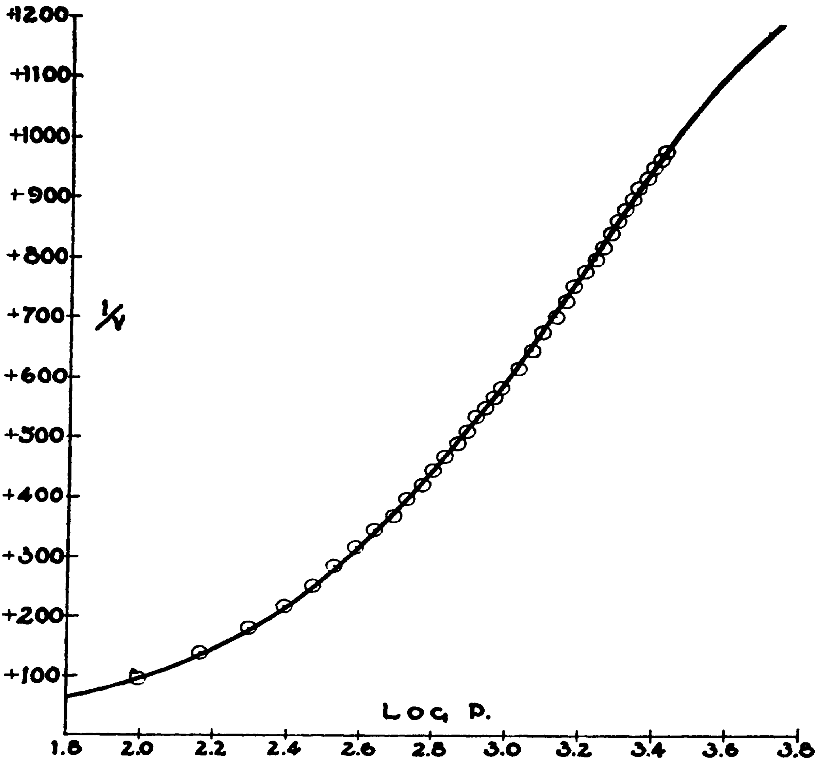


Fig. 1. Hydrogen Gas at 0°C.

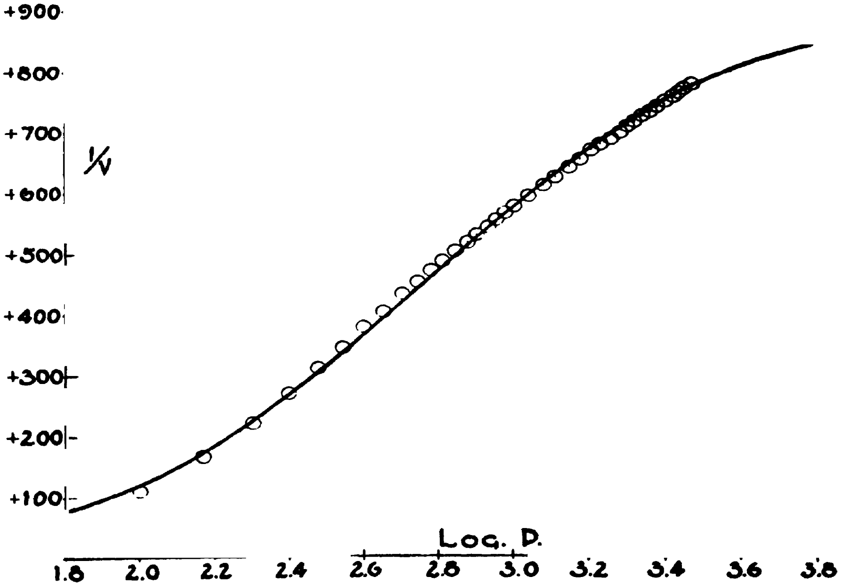


Fig. 2. Oxygen Gas at 0°C.

TABLE 2

Oxygen gas

P	*T* = 0°C		*T* = 15 6°C		*T* = 99 5°C		*T* = 199 5°C	
	1/*V*	*K*	1/*V*	*K*	1/*V*	*K*	1/*V*	*K*
atm								
1	1		0 9459		0 7329		0 5778	
100	107 9	1 043	99 6	1 036	72 7	1 016	83 3	1 011
150	164 2	1 058	151 2	1 049	108 5	1 022	110 0	1 015
200	218 8	1 068	201 1	1 058	142 9	1 027	135 1	1 017
250	268 4	1 075	246 7	1 064	175 6	1 031	159 2	1 019
300	311 7	1 079	287 9	1 068	206 5	1 033	182 1	1 020
350	348 6	1 080	324 0	1 070	234 9	1 035	204 0	1 021
400	380 4	1 080	355 6	1 071	261 1	1 036	224 6	1 022
450	408 2	1 080	383 0	1 071	285 5	1 037	243 9	1 022
500	432 5	1 079	407 5	1 070	308 3	1 038	262 5	1 023
550	453 7	1 077	429 2	1 069	329 5	1 038	280 1	1 023
600	472 5	1 075	448 8	1 068	348 8	1 038	296 6	1 023
650	489 7	1 073	466 4	1 066	366 7	1 038	312 3	1 024
700	505 3	1 072	481 9	1 065	383 1	1 038	327 2	1 024
750	519 5	1 070	497 3	1 064	398 7	1 037	341 4	1 024
800	532 2	1 068	510 5	1 062	413 7	1 037	355 6	1 024
850	543 2	1 066	523 3	1 061	427 7	1 037	367 9	1 024
900	555 6	1 065	534 5	1 060	440 9	1 037	380 4	1 024
950	566 3	1 064	546 1	1 059	453 3	1 036		——
1000	576 4	1 062	555 6	1 057	464 9	1 036		
1100	594 5	1 060	574 7	1 055	——	——		
1200	611 6	1 059	592 1	1 053				
1300	627 4	1 058	607 9	1 052				
1400	642 3	1 058	623 0	1 052				
1500	655 3	1 057	636 5	1 051				
1600	667 8	1 057	649 4	1 051				
1700	679 3	1 057	660 7	1 051				
1800	690 3	1 057	671 8	1 051				
1900	700 8	1 058	682 6	1 051				
2000	710 2	1 058	692 5	1 051				
2100	719 4	1 059	702 2	1 052				
2200	728 0	1 060	711 2	1 053				
2300	736 4	1 061	719 4	1 054				
2400	744 3	1 062	727 8	1 055				
2500	752 2	1 064	735 3	1 056				
2600	759 6	1 065	742 9	1 057				
2700	766 9	1 068	750 8	1 059				
2800	774 0	1 070	757 9	1 061				
2900	791 3	1 073	765 1	1 063				
3000		——	771 6	1 065				
				——				
		Av =		Av. =		Av =		Av =
∞	920 0	1 066	920 0	1 058	920 0	1 034	920 0	1 021

TABLE 3

Nitrogen gas

P	T = 0°C		T = 16 0°C		T = 99 5°C		T = 199 5°C	
	1/V	K	1/V	K	1/V	K	1/V	K
atm 1	1		0 9446		0 7329		0 5780	
100	100 9	1 031	94 2	1 026	103 5	1 015	80 6	1 006
150	148 5	1 040	138 7	1 033	134 3	1 018	104 9	1 008
200	192 5	1 044	179 5	1 038	162 6	1 015	127 6	1 009
250	230 9	1 047	216 0	1 041	188 6	1 020	148 9	1 009
300	264 1	1 048	247 8	1 041	212 6	1 021	168 9	1 010
350	292 9	1 047	276 2	1 041	234 5	1 020	187 6	1 010
400	318 3	1 046	301 0	1 041	254 9	1 020	205 1	1 009
450	340 1	1 045	322 8	1 039	273 6	1 020	221 5	1 009
500	359 7	1 043	342 7	1 038	291 0	1 020	237 1	1 009
550	377 1	1 041	360 4	1 037	306 9	1 019	251 7	1 009
600	393 2	1 039	376 4	1 035	321 7	1 019	265 5	1 009
650	407 8	1 038	391 2	1 034	335 6	1 018	278 6	1 008
700	421 2	1 036	404 9	1 032	348 3	1 017	291 1	1 008
750	433 5	1 035	417 2	1 031	360 4	1.017	303 0	1 008
800	445 0	1 034	428 8	1 030	371 8	1 016	314 1	1 007
850	455 6	1 032	439 8	1 029	382 3	1 015	324 8	1 007
900	465 3	1 031	449 6	1 028	392 9	1 014	334 8	1 007
950	474 6	1 030	459 1	1 027				
1000	483 3	1 029	468 2	1 026				
1100	499 1	1 027	485 0	1 024				
1200	513 9	1 025	500 0	1 023				
1300	527 3	1 024	514 1	1 022				
1400	539 7	1 023	527 1	1 021				
1500	551 4	1 023	539 4	1 021				
1600	562 3	1 023	550 1	1 021				
1700	573 1	1 023	560 5	1 021				
1800	583 3	1 024	570 8	1 021				
1900	592 3	1 024	579 9	1 021				
2000	601 1	1 025	588 6	1 022				
2100	609 4	1 026	597 0	1 022				
2200	617 3	1 027	605 0	1 023				
2300	624 6	1 028	612 7	1 024				
2400	631 5	1 029	619 8	1 025				
2500	637 7	1 029	626 6	1 026				
2600	643 9	1 030	633 3	1 027				
2700	649 8	1 031	639 4	1 028				
2800	655 7	1 033	645 4	1 029				
2900	665 8	1 039	651 0	1 030				
3000	667 1	1 036	656 8	1 032				
		Av. =		Av. =		Av. =		Av. =
∞	800 0	1 032	800 0	1 029	800 0	1 018	800 0	1 007

TABLE 4

Air

P	T = 0°C		T = 15 7°C		T = 99 4°C		T = 200 4°C	
	1/V	K	1/V	K	1/V	K	1/V	K
atm 1	1		0 9453		0 7329		0 5766	
100	102 8	1 035	95 6	1 029	71 3	1 014	81 4	1 009
150	152 4	1 044	141 8	1 038	104 8	1 018	106 0	1 010
200	198 0	1 050	184 3	1 043	136 3	1 020	129 3	1 011
250	238 3	1 053	222 0	1 045	165 5	1 022	151 0	1 012
300	273 4	1 054	255 6	1 047	192 5	1 023	171 5	1 012
350	303 3	1 054	285 7	1 048	219 6	1 024	190 8	1 012
400	329 4	1 053	311 6	1 047	240 6	1 025	209 0	1 012
450	352 5	1 052	334 3	1 046	261 6	1 025	226 1	1 012
500	373 1	1 050	354 4	1 044	280 7	1 024	242 3	1 013
550	391 7	1 049	373 1	1 043	298 2	1 023	257 5	1 012
600	408 2	1 047	390 2	1 042	314 8	1 023	272 0	1 012
650	423 2	1 045	405 8	1 041	330 5	1 023	285 5	1 012
700	437 1	1 044	420 0	1 040	344 8	1 022	298 4	1 012
750	449 4	1 042	432 5	1 038	358 4	1 022	310 7	1 012
800	461 3	1 041	444 5	1 037	371 2	1 021	322 4	1 012
850	472 6	1 040	455 8	1 035	383 3	1 021	333 3	1 011
900	482 9	1 039	466 4	1 035	394 2	1 020	344 5	1 011
950	492 6	1 038	476 0	1 033	404 4	1 020	353 6	1 010
1000	502 0	1 037	485 4	1 033	414 2	1 019		
1100	515 7	1 033	502 0	1 031				
1200	531 1	1 031	517 3	1 029				
1300	545 3	1 031	531 9	1 028				
1400	558 2	1 030	545 3	1 028				
1500	570 1	1 029	557 6	1 028				
1600	581 2	1 028	569 2	1 027				
1700	591 5	1 029	579 7	1 027				
1800	601 7	1 029	590 0	1 027				
1900	610 9	1 030	599 5	1 028				
2000	620 0	1 030	608 6	1 028				
2100	628 7	1 031	613 9	1 026				
2200	636 9	1 033	625 8	1 030				
2300	645 0	1 034	633 7	1 031				
2400	652 1	1 035	641 2	1 032				
2500	659 4	1 037	648 5	1 033				
2600	666 7	1 039	655 7	1 035				
2700	673 6	1 041	662 3	1 036				
2800	680 5	1 043	668 9	1 038				
2900	687 3	1 046	675 4	1 040				
3000	694 0	1 049	682 1	1 043				
		Av. =		Av. =		Av. =		Av. =
∞	822 0	1 040	822 0	1 035	822 0	1 022	822 0	1 012

large scale $1/V_P$ against log P, for at this point, $kP^K = 1$. This may be verified by taking the second derivative of $1/V$ with respect to log P, and

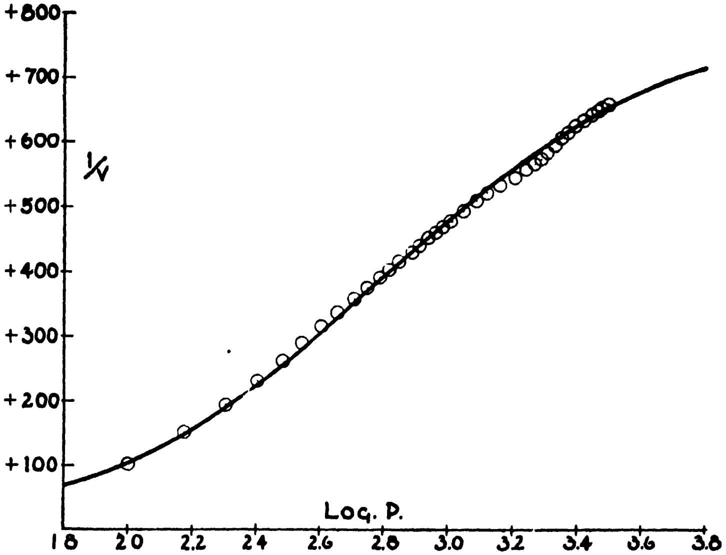


Fig. 3 Nitrogen Gas at 0°C

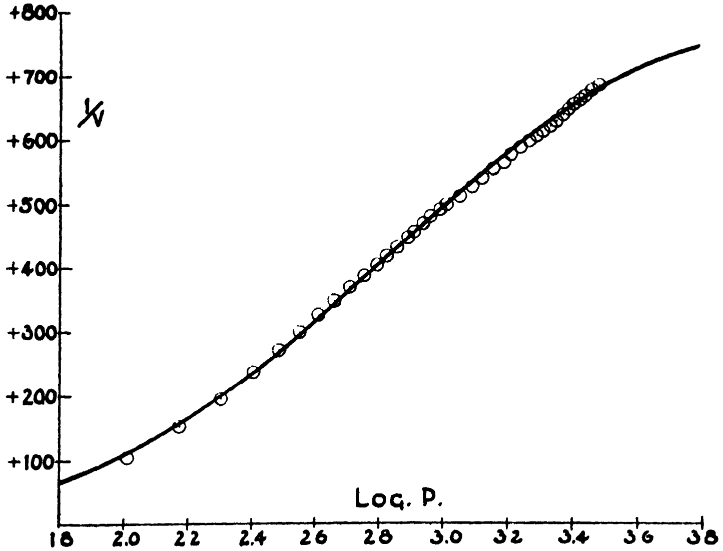


Fig. 4. Air at 0°C.

placing the resulting expression equal to zero. Hence, by equation 1, $1/2V_\infty = 1/V$ at inflection, which can be easily located from the perfect symmetry of the curve. Only one curve for each gas is given, since they are all of the same general trend and of nearly equal accuracy. V_∞ may also be obtained approximately from density measurements of the given substance in its solid state near the absolute zero of temperature, since V_∞ is practically independent of temperature and pressure. However, the inflection point method is preferable, for density measurements at extremely low temperatures are not likely to be generally reliable.

The gases chosen for this study are hydrogen, oxygen, nitrogen and air. As the most complete P- V- T data (2) available are those of Amagat, ranging from 0°C. to 200°C. and from 1 atmosphere pressure to 3000 atmospheres pressure, these data were used in the calculation of K.

RESULTS OF CALCULATIONS

The data for hydrogen gas are those of tables 4 and 8 of the original article cited above; for oxygen gas, of tables 4 and 7; for nitrogen gas, of tables 5 and 9; and for air, of tables 5 and 10

TABLE 5

Variation of K with the absolute temperature a summary

T	HYDROGEN	OXYGEN	NITROGEN	AIR
273	0 994	1 066	1 032	1 040
290	0 995	1 058	1 029	1 035
373	0 996	1 034	1 018	1 022
473	0 997	1 021	1 007	1 012
∞	1 000	1 000	1 000	1 000

DISCUSSION OF THE CONSTANTS

The concordance of the constants in each of the sixteen sets of results is quite remarkable and justifies the assumption that at 1 atmosphere pressure Charles' Law is valid. It is also of considerable interest to note that with rise in temperature of the gas the constant, K, in every case approaches unity (see figure 5) This phenomenon is in accord with the kinetic theory of gases, leading to the simple expression, $PV = $ a constant. The conditions postulated by the kinetic theory can be fulfilled only at high temperature and at moderately low pressure, in which case equation 4,

$$(V_1 - V_\infty)/(V_P - V_\infty) = P^K$$

reduces to $PV = $ a constant, since at high temperatures and low pressures K approaches, in all cases, unity, and V_∞ becomes negligibly small as compared with either V_1 or V_P.

It may be noted that K for hydrogen approaches unity from below, while in the other cases K approaches unity from above. This phenomenon is shown on figure 5, where K is plotted to four significant figures against the absolute temperature.

In conclusion, it may be pointed out that equation 4 is an empirical one, in that y of the general equation is replaced by $1/V$ without any theoretical reason for doing so. The general equation, however, does possess a theoretical foundation, since, as will be shown in a subsequent paper, it is based upon the law of mathematical probability. Furthermore, equation 4 is not intended either for extrapolation or interpolation purposes, for, as stated in the first paragraph of this article, the writer is merely endeavoring to show that the equation,

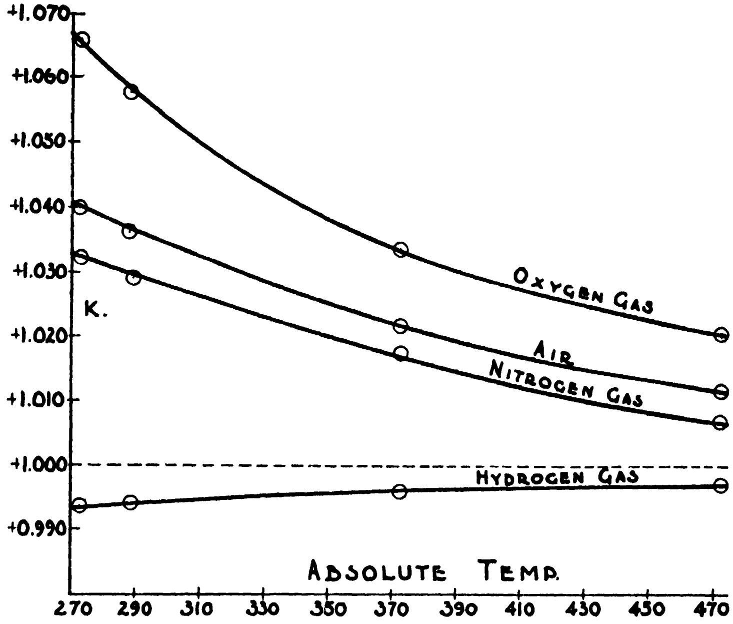


FIG. 5. RELATION OF K TO T

$$y = y_\infty kx^K/(1 + kx^K)$$

describes the general trend of a vast variety of natural processes in the fields of chemistry, physics, botany, biology, bacteriology and sociology, and even in practical engineering; for example, the depreciation and the life expectancy of physical property.

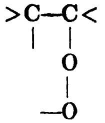
REFERENCES

(1) LINHART: J. Phys. Chem. **36**, 1908 (1932).
(2) AMAGAT: Ann. chim. phys. **29**, 68 (1893). Extensive work in this field is contemplated by Mitchells: Proc. Roy. Soc. London **A1930**, 127–258.

COMMUNICATIONS TO THE EDITOR

THE INITIAL ACT IN AUTO-OXIDATION

In a recent paper in This Journal (J. Phys. Chem. **37**, **209** (1933)), it might have been pointed out that the viewpoint of Staudinger and Lautenschläger (Ann. **488**, 1 (1931)) is not regarded as conflicting with the general theory advanced by the writer. When oxygen adds to a C═C bond through pairing of the odd electrons of the oxygen molecule with two of the electrons from the double bond, it seems reasonable to suppose that, at the instant of formation, the excess energy of the peroxide molecule would reside in these newly established electron pairs. The above authors attempt to represent this energy-rich molecule by an ordinary structural formula, showing one of the bonds actually open.



$$\begin{array}{ccc} >C & - & C< \\ | & & | \\ & & O \\ & & | \\ & & -O \end{array}$$

In the opinion of the writer, such a structure should be regarded merely as an attempt to express in terms of time-honored artifices, a fact which does not lend itself to accurate description in these terms. If, for some purposes, however, a conventional structure must be assigned, probably the one of Staudinger and Lautenschläger is more satisfactory than any other.

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INDUCED REACTIONS AND THE HIGHER OXIDES OF IRON

Remarks Upon a Paper by D. R. Hale

Hale (J. Phys. Chem. **33**, 1633 (1929)) published in 1929 a study under the above title which contains a careful and objective analysis of numerous works in this field. Among these Hale has occupied himself with my work in this field and has found himself in agreement with my experiments with regard to the autoxidation of ferrous iron (Manchot: Z. anorg. Chem. **27**, 420 (1901); Ber. **65**, 98 (1932)). On the other hand, he is of a different opinion with regard to the oxidation of ferrous iron by means of hydrogen peroxide in presence of potassium iodide as acceptor, in so far as he finds that here not two but three equivalents of free iodine occur per atom of iron.

In his discussion of this difference we find on p. 1651 the following sentence: "Unfortunately, he (Manchot) omitted to state how much ferrous iron, or what proportion of ferrous iron to acceptor, was used."

This remark is the result of a misunderstanding which was discovered in the course of a personal conversation with Mr. Hale, who was so good as to visit me in Munich in the summer of 1930 on the occasion of an European journey made by him. The work in question (Manchot and Lehmann: Ann. **460**, 179 (1928)) contains a definite statement with regard to the quantity of iron employed, but only in a very short form, owing to the limited space at my disposal in the journal, as it was merely a question of confirming and repeating former results. I wrote on p. 185: "Gef. z.B. 2,4 bezw. 4,5 ccm, ber. 2,4 bezw. 4,4 1/10 Jod," where, as is obvious from the context, "ber. 2,4 bezw. 4,4 ccm. 1/10 Jod" is the quantity which equals 2 equivalents of iodine to 1 of Fe, so that the quantity of iron used in the first experiment was 1.2 cc., and in the second 2.2 cc. of 1/10 ferrous sulfate.

While in this case there was only question of a misunderstanding, I must nevertheless state emphatically that I am not in agreement with Hale's results. In this connection a full account of detailed experimental investigations will appear in the Zeitschrift für anorganische und allgemeine Chemie.

WILHELM MANCHOT.

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NEW BOOKS

Catalytic Oxidation of Organic Compounds in the Vapor Phase. By L. F. MAREK AND DOROTHY A. HAHN. American Chemical Society Monograph Series, No. 61. 428 pp New York: The Chemical Catalog Co., Inc., 1932. Price, $9.00.

The appearance of this volume seems especially timely in view of the increasing application of catalysis to the problems of organic chemistry. The broad scope of the work is indicated by the chapter headings: Introduction; catalysis; catalytic decomposition of alcohols; oxidation of alcohols to aldehydes and acids; reactions involved in the synthesis of hydrocarbons and alcohols from water gas; oxidation of methanol to formaldehyde; oxidation of gaseous paraffin hydrocarbons; oxidation and hydration of olefins and acetylene; oxidation of petroleum oils; production of hydrogen from methane; surface combustion; the cause and suppression of knocking in internal combustion engines; oxidation of benzene and its derivatives; oxidation of naphthalene; oxidation of anthracene and miscellaneous polynuclear compounds; apparatus. In the preface the authors state that they believe it best "to consider the facts regarding both the developed and undeveloped processes and to review these critically in so far as possible. The subject could have been approached from several angles, but it was believed that a consideration of the reactions involved and products formed constituted the most satisfactory method of treatment for the present purpose." The reviewer believes that the authors have admirably fulfilled their purpose and that this volume will be an important addition to the library of those interested in catalytic oxidation.

In the introductory chapter on catalysis a fairly complete picture is given of the current ideas and theories on the subject; however, a more complete discussion of the rôle that catalysts play in initiating and breaking chain reactions would have strengthened this discussion. The authors have wisely discussed such reactions as catalytic decomposition, which are so intimately related to the problem of oxidation. The chapter devoted to the cause and suppression of knocking in internal combustion engines is one of the best reviews to be found on this important and controversial subject. Very complete references are given to the literature as footnotes, including numerous references to patents. The usefulness of the book might be improved by the addition of an author index. The section on apparatus will be found very useful to those entering this important field of industry. It is the opinion of the reviewer that this volume is an important and valuable addition to the Monograph Series of the American Chemical Society.

L. H. REYERSON.

Introduction to Organic Chemistry. By ROGER J. WILLIAMS. Second edition. New York: D. Van Nostrand Co., 1931.

The revision of this text since the first edition (1927) includes more recent information on commercial processes and on certain rapidly developing fields such as carbohydrate chemistry. The author is successful in introducing many modern concepts at the earliest possible moment, building up a viewpoint which will not need to be greatly modified after advanced study. The detail is well chosen, the presentation direct, and the scheme always apparent. Although popular as a premedical text, the book is not limited in usefulness to short or special courses.

P. D. BARTLETT.

Kristallchemie der anorganischen Verbindungen. (Sammlung chemischer und chemisch-technischer Vorträge, Heft 17). By M. C. NEUBURGER. 25.5 x 16.5 cm.; 115 pp. Stuttgart: Ferdinand Enke, 1933. Price, RM. 9.70.

From the very large amount of information which has been made available by the methods of x-ray crystal analysis, it has been found possible in recent years to deduce a number of laws governing the crystalline structure of inorganic compounds. Chiefly owing to the work of V. M. Goldschmidt and L. Pauling, these rules are sufficiently well established to enable the crystalline structure and physical properties of a not too complex substance to be predicted with some degree of certainty; there is at least one case on record where the experimental verification of such a prediction has given results of considerable technical importance.

Much of Prof. Goldschmidt's work has not been easily accessible, and Dr. Neuburger's book should commend itself both to the specialist as a useful summary of the present state of the subject, and to the more general reader as a very lucid introduction. Crystal chemistry is defined as that branch of chemistry dealing with those mutual interactions of atoms and molecules which lead to the formation of numerically unlimited ordered aggregates: its aims are taken to be the prediction of the types of crystals which can be formed from given elements, and the determination of the relations between the properties of a crystal and the properties of its constituent atoms.

The problem of atomic and ionic radii is first considered; to a first approximation the atoms and ions can be regarded as rigid spheres, so that the structure types can be classified according to the ratios of the radii of the ions involved. In the succeeding chapters it is shown how this simple consideration is modified by the influence of the charges carried by the ions, by their polarization properties, and other factors. Isomorphism, polymorphism, and morphotropism are then discussed; these terms have been endued with a new precision since the advent of crystal chemistry as an exact science. The following section on chemical binding in crystals will perhaps be disappointing to the chemist who is accustomed to differentiate fairly sharply between electrovalencies, covalencies, and coordinate links; it is apparent throughout the book, however, that valency is a subordinate factor in the construction of crystals, and it is very difficult to distinguish between the various linkages merely by measurements of interatomic distances It is here that various physical properties can very usefully be employed, and in particular the relation between hardness and the strength of interatomic bonds is discussed

As the book is intended as an introduction, many fascinating topics, such as the configuration of complex ions and the structure of the silicates, are not considered in any detail, but within the limits which the author has set himself the subject is treated in a very clear and logical manner. It should be said that actual structures are not described; these are adequately dealt with in such publications as the "Strukturbericht" and Wyckoff's "Structure of Crystals " The book is practically free from misprints; an index would be a useful addition Dr Neuburger is to be congratulated on an attractive presentation of this important subject

E. G. Cox.

Die Valenz der Metalle Fe, Co, Ni, Cu und ihre Verbindungen mit Dioximen. (The Valency of the Metals Fe, Co, Ni, Cu and their compounds with Dioximes.) By ERICH THILO. 25.5 x 16.5 cm.; 71 pp. Stuttgart: Ferdinand Enke, 1932. Price, M. 6.4.

This monograph, as its title implies, deals with the metallic complexes of oximes, mainly dimethyldioxime (DH_2), with some four metals of the first transition series.

The author first discusses the valency of the metals iron, cobalt, nickel, copper, and then, using the Born-Haber cycle (Kreisprozess), obtains values for the heat of formation for univalent, divalent, and tervalent halides of the foregoing metals.

After this discussion the dioxime compounds are considered separately.

Iron. Dimethylglyoxime and ferrous salts give [Fe 2DH] which combines with ammonia or pyridine giving [Fe 2DH, $2NH_3$] and [Fe 2DH, 2py] respectively. A definite compound with ferric iron has not yet been obtained.

Cobalt. (a) In dry acetone cobaltous chloride and the glyoxime give a blue solution from which red [Co $2DH_2Cl_2$] is obtained and this passes into a more stable green isomeride. The red and green derivatives are said to be related as *cis*- and *trans*-forms and evidence is adduced in support of this conclusion. The green chloride hydrolyzes to [Co $2DH_2ClOH$], while the bromide [Co $2DH_2Br_2$] with ethylenediamine gives

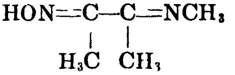
$$[H_2O\ 2DH_2\ Co\ en\ Co\ 2DH_2H_2O]^{Br_3}_{OH}$$

and with ammonia

$$[Co\ 2DH_2\ H_2O\ NH_3]^{Br}_{OH}$$

Cobalt. (b) Three types of cobaltic salts are recognized: (1) Cobalt in the cation [Co 2DH 2A] X, where A = NH_3, py, $\frac{1}{2}$en, and X = Cl, OH, NO_3, $\frac{1}{2}SO_4$, etc. (2) [Co 2DH AX] where A = NH_3, py, acridine, and X = Cl, Br, I, N_3, NO_2, SCN, OCN. (3) [Co 2DH 2X] A with cobalt in the anion, where A = H, Na, K, and X = Cl, I, NO_2, and SCN. These compounds are obtained by replacement of NH_3 in a suitable cobaltammine, e.g., [Co 2DH NH_3 Cl] from [Co $5NH_3$ Cl]Cl_2.

Nickel. In addition to the well-known [Ni 2DH], nickel forms the compound [Ni $2DH_2$]Cl_2 which has been prepared in two ways. A number of salts of the type [Ni $2DH_2$]X_2 where X is a univalent radical are described. The foregoing chloride easily forms a green hydrate [Ni DH_2 H_2O]Cl_2 which can be dehydrated; moreover, this hydrate decomposes with acetic acid, water, and alcohol in the sense 2[DH_2 Ni H_2O]Cl_2 → [Ni 2DH] + $NiCl_2$ + 2HCl + $2H_2O$. The author then passes to a consideration of the structure of [Ni 2DH] and various possibilities are discussed. In the course of this work the nickel compound of the oxime



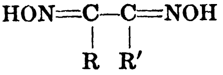
$$\underset{H_3C}{HON{=}C}{-}\underset{CH_3}{C}{=}NCH_3$$

was made.

Copper. Apart from the brown [Cu 2DH], copper chloride furnishes the bluish green [Cu DH_2 Cl_2]. The sulfate [DH_2 Cu SO_4] and phosphate [Cu DH_2 $(H_2PO_4)_2$] $\frac{1}{2}H_2O$ were also prepared. Water causes hydrolysis of these copper compounds.

$$2\ [DH_2\ Cu\ X_2] \rightleftharpoons [Cu\ 2DH] + CuX_2 + 2HX$$

Some metallic compounds of substituted dioximes are discussed,



$$\underset{R}{HON{=}C}{-}\underset{R'}{C}{=}NOH$$

where R and R′ may be OH, C_6H_5, H, $CH_3C_6H_4$, C_6H_5CO, Cl. The replacement of the hydrogen atoms in the oxime group was also considered. The concluding chapter deals with physical data such as heat of formation of the metallic halides, coördination capacity, heat of dissociation, heat of sublimation, etc.

The author has compiled an interesting little book in a rather limited field. It should, however, appeal to those interested in the coördination theory.

G. T. M. AND F. H. B.

Thermionic Vacuum Tubes. By E. V. APPLETON. 113 pp. New York: E. P. Dutton and Co., Inc., 1932. Price, $1.25.

This little book, which may be read with pleasure in an evening, might well have been called "The Physics of Vacuum Tubes." Its nine chapters are divided about equally between *internal action* of tubes and *applications;* but the applications are examples of fundamental principles rather than popular use, and include many nonradio applications. The book is strictly scientific and yet very readable, with only a moderate use of mathematics and few wasted words.

A. W. HULL.

Les Problèmes de la Biochimie Moderne. Par G. FLORENCE, Professor à la Faculté de Médecine de l'Université de Lyon, et J. ENSELME, Chief des Travaux de Chimie à la Faculté de Médecine de Lyon. 16 x 24.5 cm.; 312 pp., 8 fig. Paris: G. Doin and Co., 1932. Price, 45 fr.

The title of this book is somewhat of a misnomer. In place of calling attention to some of the major "problems" or "fields of activity" of modern biochemistry, the reviewer feels that the authors have instead presented a rather disjointed collection of more or less isolated and too brief chapters.

The book is divided into three major sections which are called "Static Biochemistry—The Biochemical Molecules," "Kinetic Biochemistry—The Agents of Chemical Activity," and "Physiological Chemistry." Static biochemistry includes chapters on the atom, colloids, surface tension, absorption spectrum in the ultra-violet, the amino acids, peptides, the constitution of the proteins, the modern view of the problem of the constitution of the hexoses, the disaccharides, the polysaccharides, the sterols, and the nucleic acids.

The section on kinetic biochemistry includes chapters on homogeneous reactions, heterogeneous reactions, pH, the membrane as a chemical agent, glutathione, constitution and mode of action of enzymes, reversability of enzyme action, the chlorophyll molecule in syntheses.

The third section on physiological chemistry includes chapters on fermentation, muscle utilization of carbohydrates, the origin of the bile salts and acids, problems of immunity, and a concluding philosophical chapter on the place of biochemistry as a special science. Two appendices follow: one having to do with biochemical nomenclature, following the recommendations of G. Bertrand as presented by him to various meetings of the "Conference Internationale de la Chimie" and the other a condensed (10 pages) statement of the three laws of thermodynamics. Author and subject indices close the volume.

The authors rightly point out that modern biochemistry requires a knowledge of organic chemistry, of physical chemistry, of physics, and of mathematics. Nevertheless, the reviewer does not feel that the brief, sketchy treatment which is accorded most of the topics discussed in these chapters is of much value either to the beginner or to the expert in biochemistry. The literature is not up to date. Only one reference to the literature of 1930 (none later) was found in the entire volume. Loeb's views of the colloidal behavior of proteins are accepted in their entirety, as is evidenced by the statement (p. 38): "The same laws which regulate the combinations of crystalloids also direct both qualitatively and quantitatively the chemical reactions of the proteins;" and later, in discussing colloids in general (p. 41), "It seems as though the specific colloidal property resides, for both hydrophobic and hydrophilic colloids, in the Donnan equilibrium." (The reviewer only wishes that colloid chemistry were as simple as that!)

The chapters on absorption spectra, the amino acids, proteins, and carbohydrates present fairly good statements of certain phases of the knowledge in these fields up to 1927 or 1928. The sterols are allowed six pages of text. The last citation is to 1929 literature. The last citation to work by Windaus is to a paper which appeared in 1913! No mention is made of ergosterol and vitamin D which is formed from ergosterol by ultra-violet radiation! But the experiments of d'Hugounenq, whereby sterols, following exposure to the air and light or to ultra-violet radiation, acquired the property of affecting the photographic plate, are given at length in spite of the fact that the weight of later evidence seems to be against such acquired photoactivity.

Glutathione is given an entire chapter. The last reference is to literature of 1927. It is discussed as a dipeptide, although it was shown to be a tripeptide in 1929. (A footnote on p. 209 states, "The recent notes tend to show that it is a tripeptide.")

The bile pigments and hemin again occupy a separate chapter. The last reference is to 1928 literature. Only a single paper by Windaus (1919) is referred to and only one by Hans Fischer (1914!), in spite of the fact that Nobel prizes were awarded both Fischer and Windaus for work in this and related fields.

In the chapter on muscle biochemistry the glucose ⇄ lactic acid theory of muscle energy is elaborated upon. The last reference is to 1928 literature. Since that time this theory has been completely overthrown and replaced by the phosphagen concept, regarding which no mention is made in the present volume. Rather interestingly, A. V. Hill is not even mentioned in connection with muscle biochemistry! Of what avail is a Nobel prize?

The authors state that problems of immunity involve *only proteins* in some particular colloidal state. They state that mineral colloids, fats, or carbohydrates do not form precipitins or give rise to specific antibodies; nevertheless it was demonstrated as early as 1926 that certain polysaccharides of bacterial origin are immunologically specific and that the specificity is of high order.

The authors do not appear to be well acquainted with English or American literature. The names of English and American scientists are frequently misspelled, *e.g.*, Dunès for Dennis, Clarck for Clark, Chieck for Chick, Mendell for Mendel, etc. No mention is made of vitamins, hormones, uronic acids, and many other groups of compounds which involve problems of modern biochemistry. There seems to be little justification for the publication in late 1932 of material obviously collected at a considerably earlier date (presumably used as a basis for a course of lectures in 1929–30) and covering a field which is changing as rapidly as is modern biochemistry.

Ross Aiken Gortner.

I. THE ADSORPTION OF THORIUM B AND THORIUM C FROM SOLUTION

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Received January 20, 1933

INTRODUCTION

Paneth (1) in his Baker Lectures has shown how, with the development of the knowledge of the chemistry of the socalled radioelements, there has come about an increasing use of these elements in studying some of the well-known chemical problems. Fajans (2), Paneth (3), and Hahn (4)[1] have made use of these radioelements in studies of the causes and mechanism of adsorption from solution. The phenomenon of adsorption is one of the most studied of chemical problems and the chemical literature is full of observations of the adsorption of many adsorbed substances by numerous adsorbents. A great deal of this work on adsorption has been carried out with difficultly defined adsorbents and with more or less complex adsorbed substances. Although these studies give valuable data because they record observations of common chemical systems as they actually exist, yet the number of variables involved makes the interpretation of the data in simple terms very difficult. The work of Fajans and others has reduced the study of adsorption to a simple system, that of a salt-like crystal as adsorbent and a single simple ion as the adsorbed substance. Because methods of analysis limit the accuracy of a quantitative study of the amount of ions removed by an adsorbent, these workers have made use of the electroscope for measuring quantitatively the number of radioactive ions which have been removed from solution. By use of this method it has been possible to measure on a rather small surface of a crystal adsorbent not only the amount of radioactive ions which have been removed from solution but also indirectly (using the radioactive ions as indicators) the amount of the ions of some of the common elements and of radicals which could not be detected in micro quantities by the ordinary methods of analysis.

From the results of the experiments just referred to, Fajans, Paneth, and Hahn have formulated rules for adsorption from solution. (For a statement and discussion of these rules see reference 2.) In these rules there is shown a relation between adsorption and mixed crystal formation, adsorption and solubility (see also Taylor and Beekley (5)) and more recently (by Fajans in his expanded rule) adsorption and weakness of dissociation of the compound formed by the adsorbed ion and the oppositely charged ion of the adsorbent.

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[1] In references 1 to 4 are to be found most of the references to work which has been done in the field of the articles to be presented.

It is the purpose of this series of three papers to report work which was started under the direction of Professor Fajans[2] in his laboratory in Munich and continued here in this laboratory, giving results which add additional information to the subject of the cause and mechanism of the adsorption of ions from solution. This first paper is to deal in general with the special technique used in all the work and to take up some of the sources of error in measurements in which the thorium B and thorium C equilibrium is concerned. The second paper will report results of the adsorption of thorium B ions on thallium bromide and iodide and the influence of different ions in the solution on this adsorption. The third paper will be concerned with the adsorption of thorium B ions on silver bromide from solutions of varying concentrations of different bromides.

Thorium B, an isotope of lead, is a desirable ion for use in a study of the adsorption of ions on insoluble halide crystals because:—

1. Its half-life of 10.6 hours permits it to be used in an adsorption experiment and then easily determined by the electroscopic method.
2. It can be very easily obtained from the emanation from a sample of radiothorium.
3. Its halides are insoluble.

For this work a β-ray electroscope was used.[3] Since the beta particles emitted from thorium B are so slow that 99 per cent of them can be absorbed by 0.4 mm. of aluminum (6), they cannot conveniently be used for determining the amount of thorium B present. From the disintegration table (7) it can be seen that from the successive disintegration products of thorium B, there are two, thorium C and thorium C_1, which emit alpha particles and two, thorium C and thorium C_2, which emit beta particles. When radioactive equilibrium has been established, the activity due to thorium C_2 is about 5 per cent of the total activity and its half-life is short enough to bring it to equilibrium quickly. The thorium C_1 comes into equilibrium instantaneously with thorium C and need not be considered as separate from it. By either alpha or beta particle measurements, then, the whole activity may be considered to be that of thorium C.

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[2] The senior author of this article (and of two to follow) takes this opportunity to express his gratitude to Professor Dr. K. Fajans, Director of the Institute for Physical Chemistry of the University of Munich, for his suggestions and his kind help and consideration in preparing the material for these papers, not only in his own private laboratory in Munich in 1928, but also while he was Baker Professor of Chemistry in Cornell University in 1930 and twice visited this laboratory.

[3] This electroscope was of design similar to that described in Ostwald-Luther's Physiko-Chemische Messungen, 4th ed., chap. 21.

From the relations given by Rutherford can be constructed (1) the activity curve for thorium B alone; (2) the activity curve for thorium B if thorium B and thorium C were in equilibrium with a constant source of thorium B and that source were removed; (3) the activity curve of thorium B if thorium B were pure at zero time and the equilibrium between thorium B and thorium C were then reached.

It can be calculated, or roughly seen from the curves, that after eight hours the course of the three curves is the same to better than 1 per cent and that after ten hours to better than 0.2 per cent. Any measurement, whether of alpha or beta particle activity after these periods of time, will indicate the amount of thorium B present to the accuracy mentioned. The measurements in the present work were made on an equilibrium mixture of thorium B and thorium C. Since with thorium B we are dealing with a lead isotope and with thorium C with a bismuth isotope, consideration will have to be given to the chemistry of these common elements. The adsorption experiments were conducted on thorium B ions, but the disintegration product, thorium C, was used to determine the amount of thorium B present. In handling the radioactive solutions, therefore, attention had to be given to all conditions which disturbed an equilibrium mixture of thorium B and thorium C ions. This first paper is to consider factors involved in the preparation and handling of the radioactive solutions for the subsequent adsorption measurements.

I. THE COLLECTION OF THORIUM B

The source of active material for the measurements, which extended over a period of three years, was a sample of radiothorium of about 3 milligram equivalence, kindly furnished us by the Welsbach Company; later to this was added another sample of 1.5 milligram equivalence procured from the University of Missouri. The emanation from this radiothorium was collected on platinum loops in the collector shown in figure 1. The scale gives the sizes of the different parts.

This collector was connected through a water resistance to a 125- or a 300-volt battery. Assuming the radiothorium is in equilibrium with thorium X and assuming that all the thorium A from the decomposition of the thorium emanation is deposited on the loops, the time for thorium B on the loops to reach equilibrium can be calculated from the decay constants. Sixty-four hours is the time required to deposit 98.4 per cent of the equilibrium amount.

II. THE PREPARATION OF RADIOACTIVE SOLUTIONS

The active deposit was dissolved off the platinum loops with nitric acid. A study was made of the rate of solution of this active deposit in 1 *N*, 0.2 *N* and 0.1 *N* nitric acid. From this study it was found that standing in 0.2 *N* nitric acid at room temperature for from five to ten minutes was sufficient to dissolve off most of the active deposit. Since the acidity of the radioactive solution had to be controlled, the amount of 0.2 *N* nitric acid used depended on the subsequent use which was made of the solution; this will be described later. This nitric acid solution was then transferred to a 100-cc. volumetric flask and made up to volume with distilled water. In order to be sure that the solution as prepared had the desired amount of activity, a 1-cc. sample was pipetted (after rinsing the pipette several times with the solution) on a watch glass and evaporated to dryness. The activity of this sample was measured by use of the beta ray electroscope and the remaining solution was then diluted with nitric acid of the same concentration to give the desired activity.

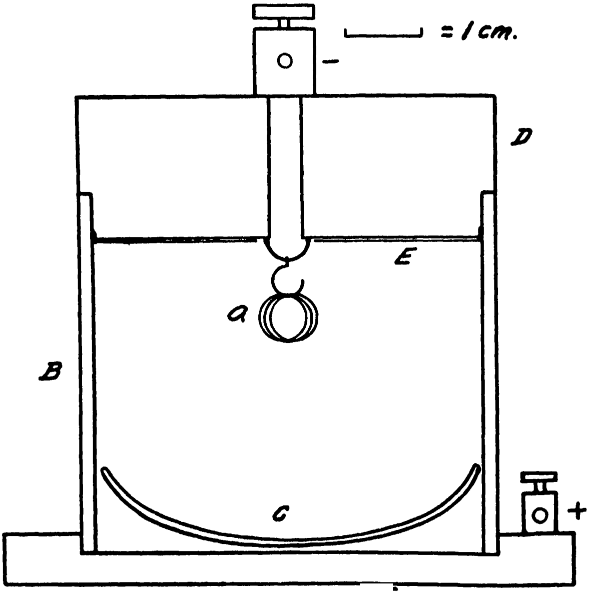

Fig. 1. Emanation Collector

A, platinum loops; B, heavy brass cylinder; C, lead dish containing radiothorium preparation (the oxide or hydroxide); D, removable wood top; E, aluminum foil cut away around the binding post; F, brass base.

The electroscope

The beta ray electroscope used was purchased through Bender and Hobein of Munich.[3] An important aid in the measurements was an eyepiece scale consisting of vertical lines bisected by a horizontal line. The gold leaf could then be timed as it passed an intersection. All samples measured were in the form of thin salt layers on 6-cm. watch glasses of slight concavity and of uniform thickness. A special watch holder and guide held the sample in the same position under the aluminum window so that reproducible results were possible It was found that the aluminum window (which was 0.07 mm. in thickness) needed to be larger than the watch glasses used because of the effect of the scattering of the beta particles. The scale of the electroscope was calibrated against the constant activity of a radioactive preparation. The natural fall of the electroscope was measured each day and this correction was made on the observed fall. To eliminate the "soaking in effect" of the insulation of the gold leaf system (an amber bead), which gives the gold leaf an abnormal natural fall after it has stood in a discharged condition for some time, the electroscope was charged up about an hour before using. The possible error due to this effect is illustrated by the following measurements:

Time elapsed since the electroscope was charged	*Natural fall of the gold leaf in scale divisions per minute*
10 minutes	0 71
34 minutes	0 63
1 hour, 3 minutes	0 51
1 hour, 43 minutes	0 50

The activities of all the samples of a set of measurements were calculated according to the disintegration formula back to the time of measurement of the first sample measured, t_0.

The acidity of the solutions

It has been observed that the acidity of the solutions plays an important part in the reproducibility of results in adsorbing radioactive ions on various materials. By controlling the acidity, the thorium B solutions could be diluted to any desired activity. For instance, two solutions of different activity were prepared and then the solution of higher activity was diluted with the calculated amount of acid to give the activity of the solution of lower activity. The measurements on both solutions are as follows:—

		Scale divisions per minute
A. Samples of solution of lower activity	1	106
	2	106
	3	107
B Samples from the solution of higher activity after it had been diluted with the calculated amount of acid	1	111
	2	108

In another experiment 10 cc. of a solution which had an activity of 68.6 scale divisions per minute (when evaporated on a watch glass) was divided into two parts, and then 5 cc. of the solution was diluted with 5 cc. of acid. This 10 cc. when evaporated to dryness had an activity of 34.5 scale divisions per minute (calculated activity would be 34.3).

It was noted at the beginning of the measurements that there was an apparent adsorption of the radioactive material on the walls of the flasks and pipettes used in the measurements. It is known that glass is negatively charged against a neutral solution and that this negative charge decreases with increasing acidity of the solution. If the adsorption of the ions is due to the charge on the glass, this adsorption should decrease with increasing acidity of the solution.

A series of glass bottles containing an equal number of glass beads were prepared. Into each was pipetted 10 cc. of a radioactive solution and varying amounts of nitric acid and water to bring the total volume up to 25 cc. These bottles were then shaken and 10 cc. of the equilibrium solution was then withdrawn and evaporated to dryness on a watch glass; the activities of the deposits on the watch glasses were immediately measured. These activities were compared with the activity of the original solution and the per cent adsorption was computed. The data follows.

	Normality of acid	*Per cent adsorption*
1	0 004	66 4
2	0 004	64 7
3	0 044	61 8
4	0 044	61 6
5	0 084	60 6
6	0 084	61 2
7	0 125	58 6
8	0 125	59 2

The same series of experiments was carried out except that the activity measurements were made after the watch glasses had stood overnight (i.e., more than eight hours).

	Activity to t_0 in scale divisions per minute
Original solution	33.1
Original solution	32.6
Normality of acid	
0.0016	31.4
0.0097	33.3
0.0097	32.4
0.0179	33.4
0.0179	32.7
0.042	32.4
0.042	33.4
0.082	34.3
0.082	33.2
0.205	34.4
0.205	34.5
0.408	34.8
0.408	34.7
0.61	32.4
0.61	32.8

These two different series of experiments indicate that there is a selective adsorption of thorium C on the walls of the glass vessels and that the increase of acidity decreases this adsorption. In the case of any adsorption of thorium B, the increase of acidity in this experiment did not change the adsorption.

The results of a third series of experiments are given in figure 2. In this series of measurements the activity of the watch glasses was followed over a period of time. Curve A represents the activity of a solution pipetted out 30 minutes after t_0 and curve B represents the activity of the same solution from a sample pipetted out 3¼ hours after t_0. Curve C represents the activity of the same solution after it had been shaken for 70 minutes in a soft glass bottle with glass beads and pipetted out 3¼ hours after t_0. The final observations are given in table 1. From this data it is obvious that thorium B is not adsorbed by the glass. The normality of the acid used in this series of measurements was 0.0016. Comparing these curves with the theoretical ones (see page 665), it can be seen that there must have been a partial adsorption of thorium C on the walls of the pipettes and on the walls of the bottles.

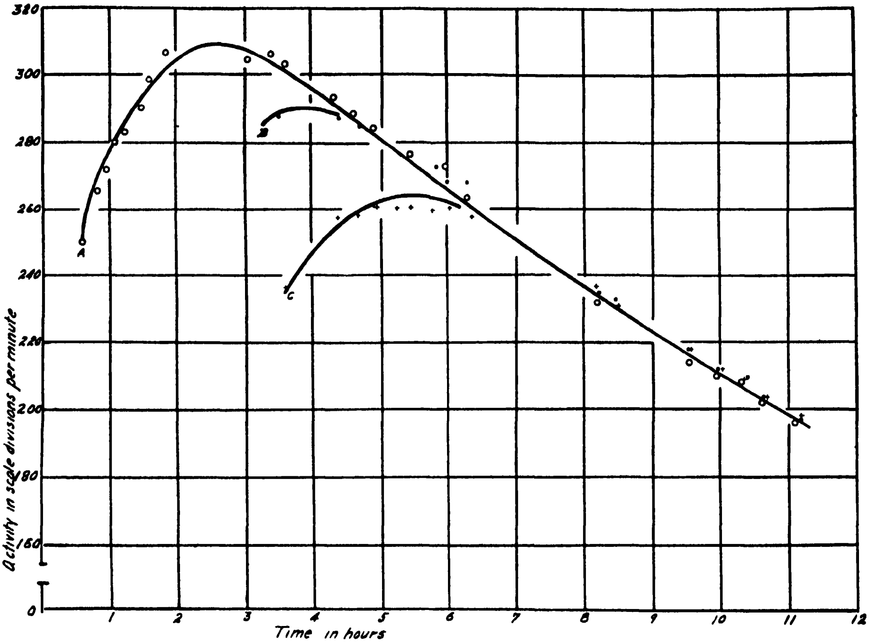

FIG 2 ADSORPTION OF THORIUM C ON GLASS

TABLE 1

SOLUTION A		SOLUTION B		SOLUTION C	
TIME	ACTIVITY	TIME	ACTIVITY	TIME	ACTIVITY
hours	*scale divisions per minute*	*hours*	*scale divisions per minute*	*hours*	*scale divisions per minute*
3 02	306				
3 37	306				
3 58	303	3 53	288	3 65	236
4 33	292	4 37	288	4 38	257
4 63	288	4 67	286	4 68	259
4 88	283	4 92	278	4 95	260
5 17	278	5 18	278	5 22	260
5 38	276	5 42	270	5 43	260
5 75	273	5 77	273	5 78	259
5 98	273	6 00	268	6 03	260
6 28	263	6 30	268	6 35	257
8 17	231	8 18	234	8 20	236
8 47	231	8 48	232	8 52	230
9 55	214	9 58	218	9 62	218
9 95	210	9 98	212	10 02	212
10 32	207	10 35	210	10 35	208
10 65	202	10 68	204	10 72	204
11 10	196	11 15	197	11 18	198

Another experiment was carried out to determine the selective adsorption of glass for thorium C. A sample of 10 cc. of an active solution was allowed to stand on a clean watch glass for 20 minutes. The glass was then rinsed with distilled water, drained, and dried on a steam bath. The decay curve for the residue on the watch glass was then determined as accurately as the weakness of the activity of the residue would permit. The times and the $\log_e$ of the activities are given in table 2. These data are plotted in figure 3. The solid line is the theoretical decay curve for thorium C.

Thus it has been shown that in the handling of the radioactive solutions there is a selective adsorption of thorium C by the glass walls of the vessels used and that this adsorption is affected by the acidity of the solution.

Herta Leng (8) has made a study of the adsorption of thorium B and thorium C on filter paper, dialyzing tubes, different kinds of glass, and paraffin. We plotted a number of her results showing the relation between hydrogen-ion concentration and the amounts of thorium B and thorium C adsorbed on different kinds of glass. The results from these curves show:—

TABLE 2

TIME	$\log_e$ OF ACTIVITY
hours	
50	1 55
70	1 43
93	1 35
1 10	1 24
1 53	1 01
1 78	85
2 17	73
2 43	53

I. For thorium C (isotope of bismuth): (1) there is a maximum adsorption at a pH of from 5 to 7; (2) the adsorption drops off rapidly around a pH of from 2 to 3.

II. For thorium B (isotope of lead): (1) there is a maximum adsorption at a pH of about 9 to 10; (2) there is a sharp dropping-off of adsorption at a pH of about 7 to 8.

It has been suggested by a number of workers that thorium B, an isotope of lead, and thorium C, an isotope of bismuth, exist in solution both in the ionic and in the colloidal condition and that the equilibrium is determined by the hydrogen-ion concentration. It is easy to understand that the colloidal form of thorium C, bismuth oxysalt, could occur in a more acid solution than the colloidal form of thorium B, some basic salt of lead. Thus the effect of the acidity on the amount of adsorption would be caused by a change in (1) the charge on the glass and its attraction for a trivalent and a bivalent ion, and (2) the nature of the radioactive material in solution.

Hahn (9) calls attention to the colloidal nature of lead, thorium B, and bismuth, thorium C, in slightly acid solutions. According to the adsorption rule thallium (thorium C_2) would be more strongly adsorbed on silver bromide than lead and lead more than bismuth. In slightly acid solutions this adsorption is just the reverse, Bi > Pb > Tl. In neutral solution this difference is more pronounced. He explains this by the supposition that in slightly acid solution bismuth and lead do not exist as ions but as so-called "radiocolloids." These radiocolloids may consist of particles of dust, decomposition particles of glass, etc., which have adsorbed the products of hydrolysis of bismuth and lead salts and behave as true colloidal particles of bismuth (thorium C) and lead (thorium B). Hahn suggests that thorium

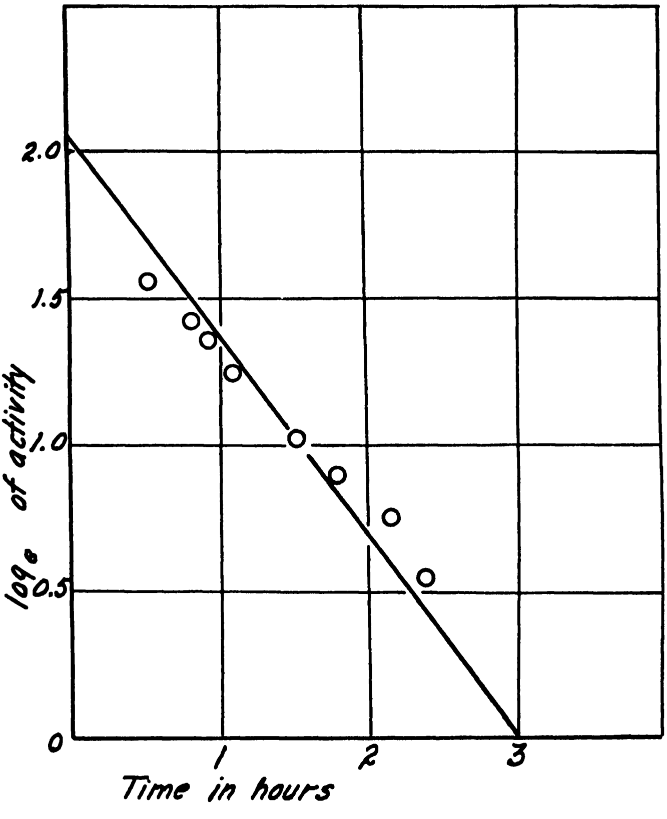

FIG. 3. DECAY CURVE FOR THORIUM C

B can be obtained in colloidal form or ionic form depending on the concentration of the acid used to dissolve it from the wire of the collector and also depending on the way that the solution is handled or diluted before adsorption is allowed to take place. He gives a series of experiments to show the possibility of the handling effect and suggests that this phenomenon warrants detailed study. The adsorption experiments take place in concentrations less than are usually considered necessary to exceed the solubility product of the salts concerned. The amount of adsorption would, in the case of these radiocolloids or pseudocolloids, depend on the number of ions in one of the particles of hydrolysis and the charge on the colloidal dust on glass decomposition particles. All of this would be a function of the hydrogen-ion concentration. The pseudocolloidal form of these two radioactive elements best explains the selective adsorption of thorium C, for it is not easy to explain this selective adsorption as due to the attraction of the negatively charged glass walls for the trivalent thorium C ion in preference to the divalent thorium B ion. Hahn was able to remove on a glass container the greater portion of the activity due to thorium B and thorium C by evaporating an active solution to dryness and then treating the residue with water.

In the following work on the adsorption of thorium B on the halides of silver and thallium, this effect was controlled by using sufficiently acid solutions to reduce this anomalous adsorption to a minimum.

SUMMARY

1. The technique used in the preparation and handling of the radioactive solutions used in the measurements in the two papers that are to follow has been described.

2. A study has been made of the selective adsorption of thorium C from a solution containing thorium B and thorium C on the walls of the glass vessels used in the work and the effect of the acidity of the solutions on this adsorption.

REFERENCES

(1) Paneth, Fritz: Radioelements as Indicators. McGraw-Hill Book Co., New York (1928).

(2) Fajans, K., and Erdey-Grúz, T.: Z. physik. Chem. **158,** 97 (1931).

(3) Horowitz, Karl, and Paneth, Fritz: Z. physik. Chem. **89,** 513 (1915).

(4) Hahn and Imre, L.: Z. physik. Chem. **144,** 161 (1929).

(5) Beekley, J. S., and Taylor, H. S.: J. Phys. Chem. **29,** 942 (1925).

(6) Rutherford. E.: Radioactive Substances and their Radiations. Cambridge University Press, Cambridge (1913).

(7) Rutherford, Chadwick, and Ellis: Radiations from Radioactive Substances. MacMillan, New York (1930).

(8) Leng, Herta: Sitzber. Akad. Wiss. Wien **11a,** 136, 19 (1927).

(9) Hahn, Otto, and Imre, Ludwig: Z. physik. Chem. **A144,** 161 (1929). See p. 172.

PHASE RULE EQUILIBRIA OF ACID SOAPS. I

Anhydrous Acid Potassium Laurate

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The question of the existence or non-existence of acid soaps, analogous to the well-known acid sodium and potassium formates and acetates, has been in debate for the last one hundred and ten years (1). The latest authority (2) reviewing the subject concludes that they do not exist.

It is easy to obtain materials which have an empirical composition showing a simple integral ratio between soap and fatty acid, as, for example, by taking the sediment from a sufficiently dilute aqueous solution, or by mixing the components in the required proportion and crystallizing them out again together; but most writers have not found it necessary to apply the ordinary thermodynamic criteria for the existence of definite chemical compounds. Hence these materials are often regarded as mixtures, whether isomorphous or heterogeneous, or as "sorption compounds," especially since Donnan and White by extrapolation of their actual observations concluded that "the separation of the acid salt NaPa,HPa is extremely doubtful, although this composition has not been covered by the experimental data."

McBain and Stewart were the first to provide some proof that an acid soap KOl,HOl is a chemical entity, in that its composition does not vary when that of the mother liquor from which it is crystallized is altered over a fairly wide range. Many acid soaps have been prepared in beautifully crystalline form; their x-ray examination has been described by Piper. A series of phase rule diagrams was worked out at the University of Bristol, England, in the years 1925–1927 and this is the first installment of the results then obtained. They are conclusive with regard to the existence and constancy of composition of acid soaps as chemical compounds.

The acid soaps are important because they, and not the free fatty acids (which are too strongly dissociated), are the common products of hydrolysis in aqueous solution. In non-aqueous solvents they are far more soluble than ordinary soaps.

EXPERIMENTAL

Materials

Lauric acid (referred to as HL), Kahlbaum, melted at 44°C. Potassium laurate (referred to as KL), specially prepared by Kahlbaum, was the same as that used by McBain and Field (3).

The systems were prepared in thick-walled Duro glass tubes about 21 cm. in length and about 1.5 cm. in diameter, which were sealed after weighing the two components into them. They were then heated to whatever temperature was necessary to transform the contents into a single, homogeneous phase. Up to 180°C. this was done in a glycerol bath, and up to 400°C. in an electric oven made by winding nichrome wire around a hollow cylinder of sheet asbestos with two transparent mica windows. A thermometer was kept touching the side of the soap tube, and heating and cooling were carried out very slowly. Stirring was effected by slowly shaking the oven as a whole, avoiding the formation of air bubbles. Carefully standardized thermometers were used throughout the investigation. On cooling these systems down to room temperature, the separation of solid crystals took place in every case from the pure fatty acid up to a concentration of approximately 75 per cent KL, 25 per cent HL; systems containing more potassium laurate than this gave rise, on cooling the isotropic liquid, to anisotropic liquid crystals; on further cooling, these were followed at a somewhat lower temperature by solid crystals.

Method of visual observation

In every case the temperature, T , at which the last trace of solid crystal disappears upon very slow heating to give either an anisotropic or isotropic liquid, was observed. The results obtained in this manner were quite reproducible up to a concentration of 75 per cent KL but above this, owing to the cloudy nature of the liquid crystals formed, there was some doubt as to the exact temperature when the last trace of solid crystalline matter disappeared, and no satisfactory results could be obtained in this manner.

The upper boundary, T_i, between the liquid crystalline phase and the isotropic solution phase was obtained by cooling the homogeneous isotropic solution until it just went turbid; this denotes the presence of a second phase, which in this case was anisotropic liquid crystals. No supersaturation was observed to occur in the separation of the liquid crystalline phase; this is in harmony with the previous phase rule studies involving the separation of the anisotropic liquid (mesomorphous) state.

It will therefore be noted that from the mode in which T_c and T_i, respectively, are observed they are free from distortion due to possible supersaturation or undercooling and that they, therefore, constitute accurately determined points on the respective phase equilibrium boundaries.

TABLE 1

Visual observations of the temperature T_c at which the last trace of solid crystal disappears on heating, and of T_i, the first temperature at which the homogeneous isotropic liquid becomes turbid or inhomogeneous on cooling

MOLE FRACTIONS		DESCRIPTION AT ROOM TEMPERATURE	T_c	T_i
KL	HL			
	1.0000	White, waxy, crystalline mass	44.0	
0.0106	0.9894	White, waxy, crystalline mass	43.7	
0.0291	0.9709	White, waxy, crystalline mass	43.3	
0.0403	0.9517	White, waxy, crystalline mass	42.7	
0.0700	0.9300	Coarse, white, crystalline mass	41.0	
0.0919	0.9081	White, crystalline mass	43.5	
0.1330	0.8670	White, crystalline mass	52.6	
0.1663	0.8337	White, crystalline mass	57.0	
0.1972	0.8028	White, crystalline mass	63.9	
0.2266	0.7734	White, crystalline mass with traces of rod or needle acid soap crystals	69.0	
0.2269	0.7731	White, crystalline mass with traces of rod or needle acid soap crystals	69.2	
0.2492	0.7508	White, crystalline mass with traces of rod or needle acid soap crystals	74.3	
0.2818	0.7182	White, crystalline mass with traces of rod or needle acid soap crystals	80.0	
0.3310	0.6690	White, crystalline mass with traces of rod or needle acid soap crystals	85.5	
0.3604	0.6396	White, crystalline mass with traces of rod or needle acid soap crystals	89.7	
0.3977	0.6023	Yellowish white, crystalline mass with traces of rod or needle acid soap crystals	93.0	
0.4123	0.5877	Yellowish white, crystalline mass with traces of rod or needle acid soap crystals	107.1	
0.4203	0.5797	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	115.0	
0.4392	0.5608	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	125.0	
0.4655	0.5345	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	144.7	
0.4951	0.5049	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	160.0	

TABLE 1—*Concluded*

MOLE FRACTIONS		DESCRIPTION AT ROOM TEMPERATURE	T_c	T_i
KL	HL			
0 5386	0 4614	Straw-colored, powdery mass	185.0	
0 5694	0 4306	Straw-colored, powdery mass	200 5	
0 6170	0 3830	Straw-colored, powdery mass	211 5	
0 6419	0 3581	Straw-colored, powdery mass	217 5	
0 6658	0 3342	Straw-colored, powdery mass	226 0	
0.7155	0 2845	Straw-colored, powdery mass	235 5	
0 7515	0 2485	Straw-colored, powdery mass	?	259 5
0 7987	0 2013	Straw-colored, powdery mass	?	305 0
0 8569	0 1431	White, powdery mass	?	358 0
0 9234	0 0766	White, powdery mass	?	374 0
1 0000	0 0000	White, powdery mass	264 0	376.0

Results of visual observation

Table 1 describes the results that have been obtained in this manner, many of which have been checked by dilatometer observations (to be described later) and by microscope examination in the small stage furnace (also to be described later). The visual method proved quite satisfactory, giving reproducible results except near the lower eutectic, where either of the other two methods was more efficient.

The complete equilibrium diagram

Figure 1 is the complete phase rule diagram for the anhydrous two-component system, containing all the observations of table 1 together with those by the methods to be described in the sequel. The heterogeneous fields are marked by lightly drawn horizontal "tie lines" whose ends represent the phases in the mixture. The heavier horizontal lines mark the eutectic temperature, the transition temperature, and the lowest temperature at which the liquid crystalline soap phase appears.

First it will be seen that the isotropic liquid phase is completely delimited by the observations T_c and T_i. It embraces the upper half of the diagram above the melting points of the pure components. The melting point of lauric acid is lowered progressively to 40°C., the eutectic point, by addition of potassium laurate. The boundary of the liquid then rises to the transition point, 91.3°C. At all temperatures below 91.3°C. crystalline acid soap KL,HL separates as pure crystals either alone as in field A, or in heterogeneous mixture with crystalline KL on the left side of the diagram in field B, or in heterogeneous mixture with crystalline HL as in the field C. We shall see that there is no evidence for solid solutions or isomorphous mixtures.

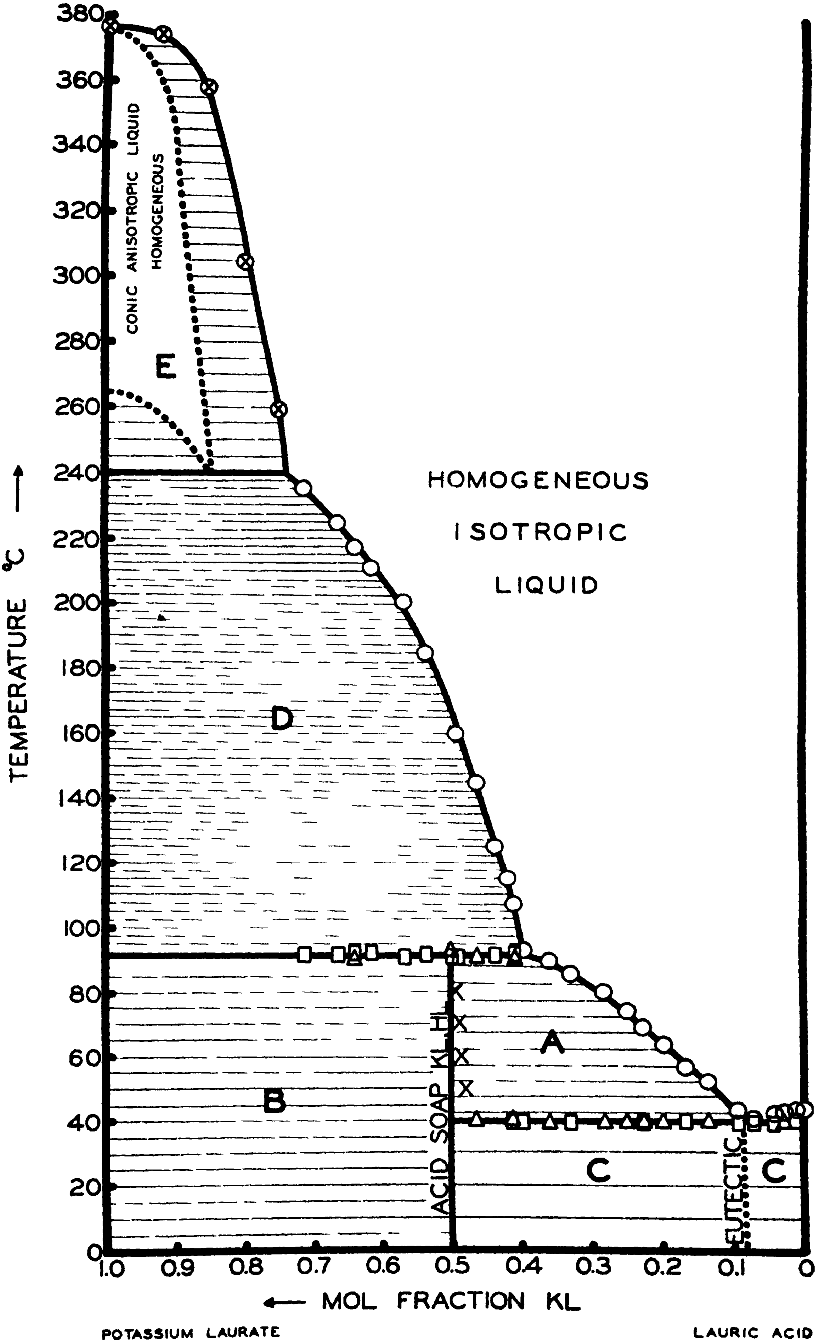

Fig. 1. The System Potassium Laurate–Lauric Acid

At 91.3°C., KL,HL exhibits a transition point, as shown also by the break in the boundary of the isotropic liquid, and breaks up completely into a mixture of that liquid with solid KL in field D. This transformation of KL,HL into liquid containing suspended KL is clearly visible. Therefore, no acid soap exists above 91.3°C. and the only one below 91.3°C. is KL,HL.

Another break in the isotropic liquid boundary is exhibited at 240°C., and inspection of the system shows that this is due to the appearance of the conic anisotropic liquid soap in field E. Whilst the boundaries of the isotropic liquid are exactly delimited even at the highest temperatures up to and including the final melting point, 376.0°C., of anhydrous liquid crystalline KL, the exact boundaries of field E have not been fixed. Above 376°C., KL and HL are completely miscible liquids.

The non-existence of isomorphous mixture and the existence of KL,HL

The extensively quoted and commonly accepted work of Donnan and White upon the anhydrous two-component system sodium palmitate–palmitic acid, alike through their imperfect method of separating liquid from solid phases and through their interpretation, has led to completely erroneous conclusions, not merely as to the position of some of the boundaries in the fragment of the diagram they chose for study, but also as to the very existence of isomorphous mixtures and of acid soaps themselves. The portion of the isotropic liquid boundary which they studied was, of course, correctly observed.

It therefore became necessary to scrutinize much more sharply the phase rule diagram just described and to obtain independent decisive evidence as to the truth of the interpretation given. Another communication will contain the complete phase rule diagram for anhydrous sodium palmitate–palmitic acid, showing the existence of two acid soaps, NaP,HP with a transition temperature of 74°C., and 2NaP,HP with a transition temperature at 91°C., and showing the non-existence of solid solutions or isomorphous mixtures in that system.

It is not easy to see with the naked eye the appearance of the first trace of liquid on heating the solid crystalline mass in field C, although the eutectic break at 40°C. is unmistakable, but progressively less distinct, as one approaches the composition KL,HL. We, therefore, turned to a dilatometric method of exhibiting the break at 40°C. which should occur at the upper boundary of the whole of the field C.

Dilatometric evidence for the absence of solid solutions

The design of the dilatometer, which was adopted after many trials, is given in figure 2. At the top of the diagram the dilatometer is exhibited in a horizontal position just after filling. This was done by attaching to a

Langmuir vacuum pump and a mercury reservoir with stopcock A closed and B open, then closing B and allowing mercury from the reservoir to fill the bulb and capillary as shown. The glass is cut at C and the position of the mercury meniscus adjusted with the dilatometer vertical, as in the lower figure, by heating the bulb to a temperature 20°C. higher than T_i at which the acid soap system becomes a homogeneous isotropic liquid, and then cooled to room temperature. Twenty dilatometers were placed in a thermostat and the expansion observed upon very slow heating (3°C. at a time, waiting twelve hours at each temperature before reading). In the neighborhood of an expected break, readings were taken at an interval of 1°C. A typical curve is given in figure 3. The break at 40°C. shows that

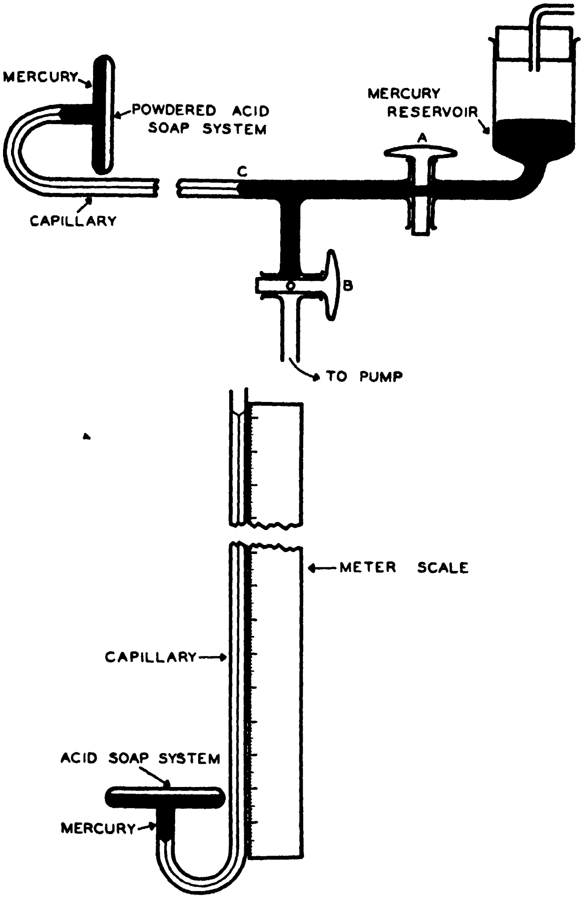

FIG. 2. DILATOMETER FOR OBSERVING CHANGES IN OR DISAPPEARANCE OF PHASES IN SYSTEMS OF LAURIC ACID WITH POTASSIUM LAURATE UP TO 0.72 MOLE FRACTION

the system contains eutectic mixture and is not a homogeneous solid solution. With one exception eutectic breaks for the nine systems occurred between 39.7°C. and 40.1°C. Where there was only 0.0106 KL the break was noted at 40.5°C. The dilatometer, therefore, proves that the system

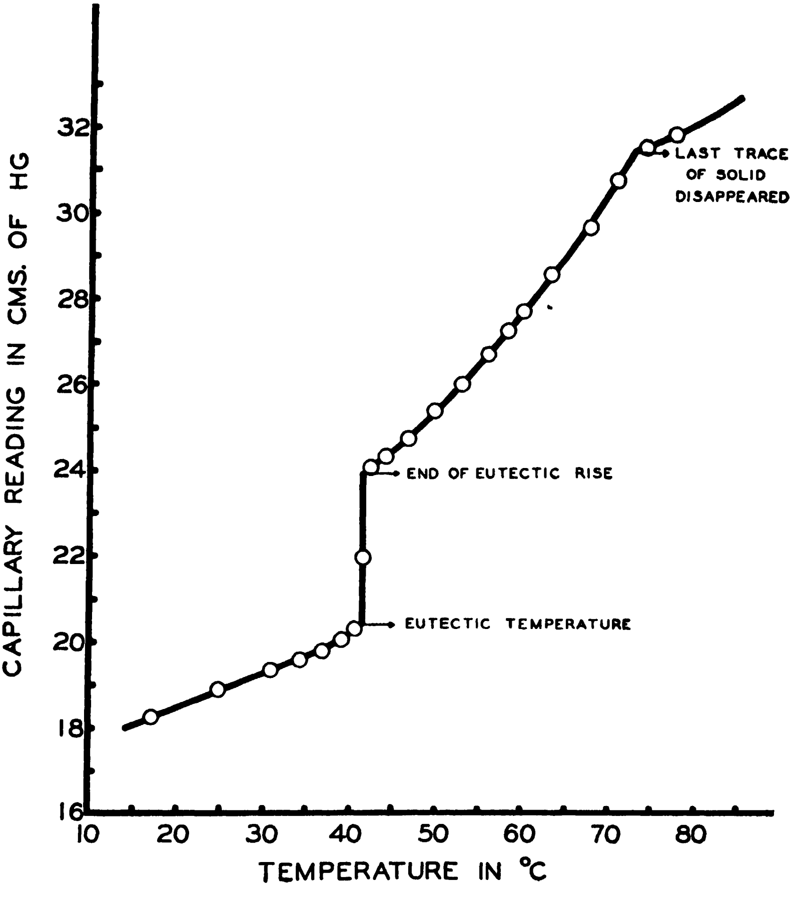

FIG. 3. DILATOMETER EXPANSION CURVE FOR A SYSTEM CONTAINING 0.773 MOLE LAURIC ACID AND 0.227 MOLE POTASSIUM LAURATE

Showing eutectic break at 40°C. and last trace of crystal disappearing at 72.5°C. (T_e).

is heterogeneous at least as far as 0.4 KL and somewhat beyond, although its indications necessarily become less distinct as the homogeneous crystalline phase KL,HL is approached.

The dilatometer for compositions containing more than 0.4 KL gives in each case a measure of the transition temperature at which the acid soap

KL, HL breaks up into its constituents. Ten readings lay between 90.5°C. and 91.5°C., confirming the interpretation of the break in the boundary of the isotropic liquid at 91.3°C.

Microscopic method

A thin layer of the powdered system between microscope slide and cover glass was examined between crossed Nicols, using an adjustable air thermostat upon the stage of the microscope. At room temperature all systems are doubly refracting, KL slightly and KL,HL strongly. The latter needle or rod-like crystals, therefore, appear very bright between crossed Nicols. On close examination the acid soap appears as elongated hexagonal plates often radiating from a point.

Upon slowly heating, the eutectic point is marked by the sudden appearance of isotropic liquid, black between crossed Nicols. As the temperature is progressively raised, the amount of isotropic liquid is seen by the proportion in which it fills the field. For example, for 0.029 KL + 0.971 HL the field became wholly black at 43.1°C., as compared with T_c = 43.3°C. observed with the naked eye. The first visible appearance of liquid in the nine systems occurred between 39.6°C. and 40.0°C., the temperature being sharply 39.8°C. for the most favorable compositions.

For the composition KL,HL, the system appears homogeneous, undergoing no visible change until 90.0°C., when the field suddenly darkens as the acid soap is transposed into slightly doubly refracting potassium laurate suspended in the isotropic liquid (black between crossed Nicols). On the other hand, when the mole fraction was 0.64 KL, the system was obviously heterogeneous, suddenly darkening at 89.9°C.

Screw press method

Donnan and White merely allowed liquid to drain away from solid matter, a process which is necessarily extremely incomplete. Here several systems in field A have been tested for heterogeneity by squeezing in a mild steel press lined with filter paper and with filter paper supported on fine mesh nickel gauze upon the perforated filter plate. The whole is maintained in the thermostat, and when the plunger is screwed down every three hours or so for several days, the isotropic oily liquid escapes. The residual hard white cake is analyzed by determination of T_c in a sealed glass tube, the composition being read off from figure 1. The composition of the cake lies close to KL, HL, showing that this is a separate pure phase. All systems heated above 91°C. yield a residue of pure KL in accordance with the results of the previous methods.

Others who have observed the acid soap KL, HL are Oudemans (1863), McBain and Eaton, Ekwall, etc. (*loc. cit.*), but this is the first time that it has been demonstrated that it is a pure chemical compound and the only one existing in this two-component system.

SUMMARY

It has been carefully demonstrated by a number of independent methods that the acid soap consisting of equal molecular proportions of potassium laurate and lauric acid is a true chemical individual that does not form solid solutions or isomorphous mixtures with either component. It exists only below 91.3°C., the transition temperature at which it decomposes into potassium laurate and the liquid mixture. There is a eutectic point between the acid soap and lauric acid at 40.0°C. and a break in the boundary of the isotropic liquid at 240°C., the lowest temperature at which anisotropic liquid exists in the two-component system.

REFERENCES

(1) *For (amongst others):* CHEVREUL, M. E.: Recherches chimiques sur les corps gras d'origine animale, pp. 34, 53, 408 (Paris, 1823); OUDEMANS, A. C., JR.: J. prakt. Chem. **89**, 206 (1863); KRAFFT, F., AND STERN, A.: Ber. **27**, 1747 (1894); McBAIN, J. W., AND TAYLOR, M.: Z. physik. Chem. **76**, 179 (1911); McBAIN, J. W., TAYLOR, M., AND LAING, M. E.: J. Chem. Soc. **121**, 621 (1922); McBAIN, J. W., AND STEWART, A.: J. Chem. Soc. **1927**, 1392; EKWALL, P.: Acta Acad. Aboensis Math. Phys. **4**, No. 6, (1927); McBAIN, J. W., AND EATON, M.: J. Chem. Soc. **1928**, 2175; SCHÜTTE, O.: Seifensieder-Ztg. **56**, 85, 93 (1929); PIPER, S. H.: J. Chem. Soc. **1929**, 234; MALKIN, T.: Ber. **B63**, 1807 (1930).

Against (amongst others): DONNAN, F. G., AND POTTS, H. E.: Kolloid-Z. **7**, 208 (1910); DONNAN, F. G., AND WHITE, A. S.: J. Chem. Soc. **99**, 1668 (1911); PROSCH, W.: Z. deut. Öl-Fett-Ind. **42**, 410, 425, 433, 449, 462 (1922); LEETEN, W.: Z. deut. Öl-Fett-Ind. **43**, 50, 65, 81 (1923); ZSIGMONDY, R.: Kolloidchemie, 5th ed., II, p. 172. Leipzig (1927).

(2) LEDERER, E. L.: Handbuch der Kolloidwissenschaft, Bd. V, "Kolloidchemie der Seifen," p. 125. T. Steinkopff, Dresden and Leipzig (1932).

See likewise Ubbelohde's Handbuch der Chemie und Technologie der Öle und Fette, Bd. III, Abt. 2, p. 748. S. Hirzel, Leipzig (1930).

(3) McBAIN, J. W., AND FIELD, M. C.: J. Phys. Chem. **30**, 1545 (1926).

THE CATALYTIC ACTIVITY OF CHROMITES FOR THE OXIDATION OF CARBON MONOXIDE[1]

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The metal oxide and mixed metal oxide catalysts for the oxidation of carbon monoxide have received considerable attention since the investigations of Lamb, Bray, and Frazer (1). Bone (2) and his coworkers studied the oxidation of carbon monoxide using nickel, copper, and their oxides. Bennett (3) studied the activity of a number of purified oxides and found manganese, nickel, and cobalt oxides to be especially active at low temperatures. Recently Engelder and Miller (4) have shown that a mixed catalyst of titania and copper oxide was active, and Engelder and Blummer (5) have shown that a catalyst composed of cobaltic and ferric oxides has a high degree of activity in a temperature range of 0°C. to 200°C. Frazer (6) has shown that a catalyst composed of ferrous chromite is active at elevated temperatures.

This paper records the results of a continuation of work upon metal chromites as catalysts for the high temperature oxidation of carbon monoxide.

EXPERIMENTAL PART

Preparation of catalysts

The chromites were prepared by two methods, the method of Gerber (7) and the method of Lazier (8). The method of Gerber is as follows: A mole of the anhydrous metal chloride was ground with a mole of potassium dichromate to a fine powder. The mixture was fused in a porcelain dish at 900°C. for one hour. The resulting mass was leached with boiling water and concentrated hydrochloric acid, and then dried. It was found impossible to prepare cupric chromite by this method, as at 900°C. the cupric chromite decomposed forming cuprous chromite, which gradually reoxidized to cupric chromite upon cooling and yielded a mixture of cupric chromite and chromium oxide.

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[1] The material in this communication is abstracted from the dissertation submitted by E. C. Lory in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Johns Hopkins University, June, 1932.

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The method of Lazier consists of the preparation of a "metal ammonium chromate" and its subsequent decomposition, forming a mixture of the metal chromite and the metal oxide. The preparation of cobaltous chromite is given as an example. One mole of cobalt nitrate dissolved in 300 cc. of water was mixed with one mole of chromic trioxide in 100 cc. of water. The resulting solution was heated to 80°C. and to it was added three moles of ammonia. The resulting dark red precipitate was filtered by suction and washed sparingly with water and dried at 110°C. The dried precipitate was decomposed by heating small quantities in a casserole over a free flame. This gave an extremely fine greenish black powder composed of an equimolar mixture of cobalt oxide and cobaltous chromite. This was leached with concentrated hydrochloric acid until the acid gave no reaction for cobalt. The resulting chromite was a fine dark green powder.

Catalytic activity of chromites

The method used in testing the catalytic activity of the chromites for the oxidation of carbon monoxide consisted in the direct comparison between the catalyst and a catalyst known to be 100 per cent efficient. The apparatus and method developed by Bennett (3) was used with slight modifications. The dried gas mixture containing 1 per cent carbon monoxide was passed over the catalyst at the rate of 100 cc. per minute. The catalyst bed was 1 sq. cm. in area and 10 cm. deep. It was contained in a glass tube so arranged that the gases were preheated before passing over the catalyst. The carbon dioxide formed was removed by passing the gas through standard barium hydroxide. The remaining gases were dried and passed over hopcalite. This quantitatively oxidized any remaining carbon monoxide, the carbon dioxide formed being absorbed in a second absorption flask. The excess barium hydroxide in the two absorption flasks was titrated with standard oxalic acid. A direct comparison of the barium carbonate present in the two flasks gave the efficiency of the catalyst and was not affected by fluctuations in the rate of flow or concentration of carbon monoxide in the testing gas. With this method good checks were obtained with a similar catalyst at identical temperatures.

Table 1 gives the results of the tests upon the various chromites, giving the temperatures at which they possess 10, 20, 40, 60, 80, 90, and 100 per cent efficiency in the oxidation of a 1 per cent carbon monoxide–air mixture.

Surface oxidation of chromites

It has been noticed by O. G. Bennett that upon heating a chromite and washing with water, the filtrate was slightly colored. It was thought that this coloration might be due to the chromic acid formed by the oxidation of the chromite during heating. Tests were made upon copper, cobalt, and nickel chromites to determine if oxidation did occur and the extent of oxidation.

Experimental procedure. A 10-g. sample of the chromite was weighed into a Gooch crucible and leached with hot water until no test for chromic acid could be obtained in the filtrate. The crucible was then heated in an electric furnace to the desired temperature. It was leached with hot water in 200-cc. portions. The amount of chromic acid was determined iodometrically by titration with 0.01 N sodium thiosulfate. In most cases three to five leachings were required to remove completely the chromate present. The results of the surface oxidation on copper, cobalt, and nickel chromites are given in table 2, showing the temperature and time (in hours) of heating, with the per cent of CrO_3 by weight obtained in the filtrate.

These results tend to show that upon the heating of a chromite the surface of the chromite is oxidized to a chromate, but that the oxidation is only on the surface. To determine whether or not it was a case of equilibrium, a sample of copper chromite No. 3 was heated in a steel bomb at 400°C. under a pressure of 55 atmospheres of oxygen for twenty-four hours. Upon being leached it showed the same amount of chromate as when it was heated at atmospheric pressure.

Reduction of surface chromate by carbon monoxide

If the formation of chromate on the surface of a chromite is the active agent in the oxidation of carbon monoxide, the reduction of the chromate must occur at, or below, temperatures at which the chromite is catalytically active. Tests were carried out upon copper and cobalt chromites to determine whether or not the chromate present on the surface of the chromite was reduced by carbon monoxide.

The method of determining the reduction by carbon monoxide was to pass carbon monoxide over the chromite and absorb the carbon dioxide formed in standard barium hydroxide. Nitrogen was used to give an oxygen-free atmosphere.

Copper chromite No. 3. Reduction of the chromate and also of the copper oxide present took place at 100°C. The amount of carbon dioxide was in considerable excess of the amount of chromate present due to the simultaneous reduction of the copper oxide. Upon leaching after reduction no chromate was found to be present.

Cobalt chromite No. 1. Cobalt chromite was studied in more detail, as the cobalt oxide was not reduced by the carbon monoxide and quantitative checks of the amount of chromate present could be obtained. Reduction was observed when the temperature of the chromite reached approximately 160°C. Upon leaching with hot water a small amount of chromate was found to remain and not be reduced by the carbon monoxide at 200°C.

TABLE 1

Efficiency of catalysts used in the oxidation of a carbon monoxide–air mixture

CATALYST	TEMPERATURES (°C) AT WHICH CATALYST HAS EFFICIENCY OF						
	10 per cent	20 per cent	40 per cent	60 per cent	80 per cent	90 per cent	100 per cent
Copper chromite*							
No. 1	30	31	33	35	46	61	94
No 2	103	125	152	168	178	183	199
No 3	44	57	74	91	118	120	142
No. 4	107	116	129	140	149	153	165
No. 5	55	78	82	84	85	87	102
Copper dichromate†							
No. 1	106	129	153	170	194	217	265
No 2	217	239	273	300	327	341	357
Cobalt chromite‡							
No 1	230	255	283	300	323	349	386
No 2	66	84	100	100	101	104	111
No. 3	147	169	196	210	222	229	243
Ferrous chromite§							
No 1	136	154	182	199	218	231	254
No. 2	216	239	248	270	304	400	—
Nickel chromite¶							
No. 1	259	283	320	353	383	398	431
Manganous chromite‖							
No. 1...	235	259	285	298	313	341	420

* Copper chromite:

No. 1. Copper chromite prepared from "copper ammonium chromate," decomposed but not leached

No. 2 Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid

No. 3. Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid and heated to 700°C.

No. 4. Copper chromite No. 3 heated in a bomb for twenty-four hours at 400°C. under a pressure of 55 atmospheres of oxygen in the hope of increasing the oxidation of the chromite to chromate

No. 5. Catalyst prepared by precipitation of cupric carbonate upon a sample of copper chromite No. 3. Heated to 170°C. for three hours with the carbon monoxide mixture passing over it, and then tested. No. 1 and No. 5 have nearly identical activities.

† Copper dichromate:

No. 1. Copper dichromate prepared by saturating a solution of chromic acid with basic copper carbonate and slowly evaporating at room temperature in a vacuum. Material heated to 250°C., cooled, and tested.

No. 2. Cupric dichromate, Eimer and Amend C. P. crystalline material, heated for eight hours at 150°C. and at 215°C. for six hours. Upon completion of testing, a Bunsen active oxygen test showed the presence of 76 per cent cupric dichromate.

‡ Cobalt chromite:
- No. 1. Cobalt chromite prepared by Gerber's synthesis.
- No. 2. Decomposition product of "cobalt ammonium chromate." Not leached.
- No. 3. Cobalt chromite from "cobalt ammonium chromate," leached with concentrated hydrochloric acid until free of cobaltous oxide.

§ Ferrous chromite:
- No. 1. Decomposition product of "ferric ammonium chromate." Not leached.
- No. 2. Ferrous chromite prepared by Gerber's synthesis

¶ Nickel chromite:
- No. 1. Nickel chromite prepared by Gerber's synthesis.

|| Manganous chromite:
- No. 1. Manganous chromite prepared by Gerber's synthesis.

TABLE 2

Surface oxidation on copper, cobalt, and nickel chromites

TEMPERATURE	TIME	PER CENT CrO_3	TEMPERATURE		PER CENT CrO_3
Copper chromite No. 3					
Test No 1			Test No 2		
degrees C	*hours*		*degrees C*	*hours*	
200	10	0 0504	130	36	0 0100
450	*1	0 0663	160	73	0 0212
330	10	0 0660	450	2	0 0651
300	2	0 0641	300	3	0 0663
300	16	0 0688	328	7	0 0693
100	250	0 0001	300	8	0 0664
Average for high values = 0.0678 per cent CrO_3					
Cobalt chromite No. 1					
Test No 1			Test No 2		
450	6	0 0728	300	18	0 0680
300	6	0 0623	500	5	0 0728
300	11	0 0720	530	5	0.0734
200	12	0 0332	900	6	0 0730
500	7	0 0730	160	1168	0 0102
Average for high values = 0.0738 per cent CrO_3					
Nickel chromite No. 1					
Test No 1			Test No 2		
430	5	0 0251	500	11	0 0256
460	5	0 0252	500	3	0 0240
410	3	0 0262	675	3	0.0241
400	84	0 0276	500	12	0 0236
530	73	0 0244	500	10	0.0262
800	3	0 0261	800	3	0 0253
Average for high values = 0.0260 per cent CrO_3					

The results of the reduction of cobalt chromite are given in table 3, giving the number of cubic centimeters of 0.01 *N* thiosulfate solution required to titrate the chromate present.

TABLE 3

Results of the reduction of cobalt chromite

TEST NO 1		TEST NO 2	
Chromate by leaching	22 61 cc.	Chromate by leaching	22 05 cc.
Chromate by reduction	23 33 cc	Chromate by reduction	21 79 cc.
Chromate by reduction	22 81 cc.	Chromate by reduction	19 41 cc.

These results indicate that the chromate formed upon the surface of the chromite is reduced by carbon monoxide at the same temperatures at which the chromites become catalytically active.

Adsorption of DuPont Scarlet 2RL by chromites

Paneth and Vorwerk (9) have shown that Ponceau 2R is adsorbed on the surface of crystalline lead sulfate apparently in a monomolecular layer, and by adsorbing it on a surface of known area they have calculated the area occupied by one molecule of the dye when it is adsorbed upon the surface of lead sulfate. The adsorption of the dye upon copper, cobalt, and nickel chromites has been measured. In these experiments DuPont Scarlet 2RL was used, as it is the same dye chemically as Ponceau 2R.

TABLE 4

Adsorption of DuPont Scarlet 2RL upon chromites

CHROMITE	WEIGHT OF DYE ADSORBED BY 1 GRAM OF CHROMITE × 10^4 GRAMS	MOLES OF DYE ADSORBED BY 1 GRAM OF CHROMITE × 10^7	NUMBER OF MOLECULES OF DYE ADSORBED × 10^{-17}	SPECIFIC SURFACE OF CHROMITES × 10^{3} SQ CM
$CuCr_2O_4$ ..	5 71	11 89	7 21	14 38
$CoCr_2O_4$..	9 63	20 05	12 15	24 23
$NiCr_2O_4$. ...	2 20	4 58	2 78	5 54

The method used was that of Paneth and Vorwerk. One and one-half grams of chromite was weighed into an ampoule of about 15 cc. capacity. Ten cubic centimeters of the dye solution was admitted with a pipette, the ampoule sealed, shaken for an hour and then centrifuged. Ten solutions of increasing concentration were used to obtain an adsorption isotherm at room temperature. Five cubic centimeters of the clear supernatant liquid was pipetted out and diluted to a dilution easily read upon the colorimeter. The comparison was made by means of a Bausch and

Lomb colorimeter. The results of the adsorptions of DuPont Scarlet 2RL upon the chromite are shown in table 4.

Owing to the high concentration of dye necessary to reach saturation of the surface and the attendant difficulties in determining the amount adsorbed, the results given in table 4 are not accurate to better than 10 per cent.

Combining the amount of surface found by dye adsorption with the amount of chromic acid found by leaching, the area occupied by each chromium atom can be calculated. The results are shown below.

	Area occupied by each chromium atom on the surface
Cobalt chromite	5.49×10^{-15} sq. cm.
Nickel chromite	3.52×10^{-15} sq. cm.
Copper chromite	3.50×10^{-15} sq. cm.

X-ray diffraction patterns were taken of cobalt, copper, and nickel chromites to determine whether or not the chromites prepared in this investigation were true chromites or mixtures of the oxides. Powder diagrams showed them to be definite compounds and not mixtures. Copper chromite was apparently not a cubic lattice and the x-ray investigation of this compound is being continued.

DISCUSSION

There are two possible explanations for the activity of the chromites in the oxidation of carbon monoxide: (1) the adsorption of the carbon monoxide with its activation through adsorption, or (2) the adsorption and activation of the oxygen. From the results of the surface oxidation of the chromites and the reduction of the chromate formed it would seem more logical that the activity is due to the adsorption of oxygen to form a chromate and its activation through a chemical formation. The activation of the saturated oxygen molecule would seem to be the more important factor, rather than the activation of the unsaturated carbon monoxide molecule.

The activity of the decomposition product of the "metal ammonium chromate" appears to be due to the presence of the metal oxide. When this mixture is leached with acid the oxide is removed, and the activity is then due to that of the chromite.

The oxidation of the chromites to chromate seems to be limited to a surface reaction, as increased heating under high pressure of oxygen did not increase the amount of chromate formed. The chromate appears to form a surface film that prevents further oxidation.

Studies of the adsorption of carbon monoxide, oxygen, and carbon dioxide by the chromite and chromate surfaces are now being carried out.

SUMMARY

1. The catalytic activity of copper, cobalt, nickel, manganous, and ferrous chromites for the oxidation of carbon monoxide has been determined.

2. It has been shown that upon heating the chromites are oxidized to sexivalent chromium on the surface, the surface film preventing further oxidation.

3. The chromate formed on the surface of the chromite is reduced by carbon monoxide at, or below, the temperatures of catalytic activity of the chromite for oxidation of carbon monoxide.

4. The specific surface of the chromites was determined by the method of Paneth and Vorwerk through adsorption of DuPont Scarlet 2RL.

5. An explanation of the activity of the chromites for the oxidation of carbon monoxide through the formation of a surface compound has been proposed.

The writer wishes to express here his appreciation to Professor J. C. W. Frazer, at whose suggestion and under whose supervision the work described was carried out.

He also wishes to thank Dr. O. G. Bennett for supplying him with a sample of ferrous chromite and for his helpful criticism during this investigation.

REFERENCES

(1) LAMB, BRAY, AND FRAZER: Ind. Eng. Chem. **12**, 213 (1920).
(2) BONE AND ANDREW: Proc. Roy. Soc. London **A110**, 16 (1926).
(3) BENNETT, O. G.: Dissertation, The Johns Hopkins University, 1930.
(4) ENGELDER AND MILLER: J. Phys. Chem. **36**, 1345 (1932).
(5) ENGELDER AND BLUMMER: J. Phys. Chem. **36**, 1353 (1932).
(6) FRAZER, J. C. W.: U. S. patent 1,789,812, January 20, 1931.
(7) GERBER: Bull. soc. chim., New series, **27**, 435 (1877).
(8) LAZIER: British patent 301,806, June 12, 1926; U. S. patent 1,746,783, February 11, 1930.
(9) PANETH AND VORWERK: Z. physik. Chem. **101**, 480 (1922).

THE SOLUBILITY OF THIOUREA IN WATER, METHANOL, AND ETHANOL

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INTRODUCTION

Solubility data on thiourea, an analogue of urea, in water is limited to a few isolated temperatures (4, 8, 11, 12). No previous determinations on the solubility of thiourea in water, in methanol, or in ethanol over a temperature range have been made. Such data are of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

MATERIALS

The thiourea used was obtained from the Eastman Kodak Company and was their best grade. It was purified by recrystallization three times from water. The final product had a melting point of 181.4°C., which was slightly below that recorded in the literature (6).

A portion of the above thiourea was further purified by two recrystallizations from c.p. methanol. The final product showed a melting point of 181.4°C., which was the same as that of the sample after the third water recrystallization.

The purity of the thiourea was checked by chemical analysis for its sulfur, nitrogen, and thiourea content. It was felt that the data from analysis would be more reliable than the melting point determinations, because of the decomposition of thiourea at its melting point.

The first sample showed an average sulfur content of 42.10 per cent for twelve determinations (eight by a sodium peroxide oxidation (3), and four by a nitric acid–bromine oxidation (13, 19)), with maximum deviations from the average of 0.07 per cent. The second sample (methanol recrystallization) showed an average sulfur content of 42.14 ± 0.04 per cent for three determinations (3). The nitrogen content of the thiourea samples, determined by the Gunning method (2) showed 36.79 ± 0.03 and 30.80 ± 0.2 per cent. The thiourea content, determined by the method employed by Kappana (7) as recommended by Reynolds and Werner (14) and modified by Werner (21), showed 99.97 ± 0.04 per cent and 99.98 ± 0.02 per cent for the water-recrystallized and methanol-recrystallized samples.

Boiled distilled water was employed in all determinations where water was the solvent. Baker's C. P. absolute methanol was twice refluxed with lime for six hours and then distilled through a six-bulb Le Bel-Henninger column. That portion boiling within 64.63 ± 0.01°C. (corr.) was collected and used in the solubility determinations. Pure grain alcohol was twice refluxed with lime for over six hours and distilled as under methanol. The distillate boiling within 78.43 ± 0.02°C. (corr.) was collected and used for the solubility determinations. The procedure for ethanol was essentially that of Merriman (9).

PROCEDURE AND APPARATUS

The synthetic method of Alexejew (1) was employed in making the solubility determinations. This method consisted in heating weighed quantities of solvent and solute in a sealed tube, rotated in a water bath, and noting the temperature at which the solid phase had nearly disappeared. In recent years other investigators (16, 17, 18, 20) have found this method to be accurate and a reliable means for determining the solubility of solids in various solvents. As pointed out by these investigators, care must be taken in attaining true equilibrium conditions at the solubility temperature; this can ordinarily be obtained through slow heating and using low rates of temperature rise. A temperature rise of 0.01°C. per minute was used in some cases, though in many cases thermostating for a period of time was employed. Sunier (17) pointed out that with a rate of heating of 0.01°C. per minute, results well within 0.1°C. of the true solubility temperature were obtained for naphthalene in aliphatic alcohol systems. The author feels that this same degree of accuracy would hold for the systems studied in the present research.

The results obtained by the synthetic method are necessarily under different pressures. This question has been given extensive theoretical and practical consideration. Although it is possible that extremely high pressures would exert an influence, statements (15) are found that under ordinary conditions in which the pressure does not exceed ten atmospheres, no noticeable effect on solubility would be produced. No abnormalities in the solubility curves obtained by this method have been attributed to variation in pressure. The apparatus used has been described earlier (17).

Other investigators (16, 17, 18, 20) have shown that the size of the crystal is of importance in attaining true equilibrium conditions. The method was that ordinarily employed and consisted in rapidly heating the tube to a temperature where all the solute dissolved, and then cooling rapidly with vigorous shaking.

Thin wall Pyrex tubes of 7 mm. internal diameter and approximately 14 cm. long were used. The tubes were cleaned with sulfuric–chromic acid cleaning solution, rinsed with distilled water, and then heated over an open

Bunsen burner to dull redness, placed in a desiccator, allowed to cool, and weighed. For marking the respective tubes, they were first coated with paraffin, the desired identification marks inscribed with a steel pen, and hydrofluoric acid (48 per cent) added. After five minutes, the paraffin was dissolved off with acetone, and the tube prepared as described above.

In these determinations a thermometer certified by the Bureau of Standards was employed. The thermometer could be read to ± 0.01°C. with the aid of a magnifying glass. The temperatures recorded should be accurate to ±0.02°C.

Some preliminary data was obtained for the possible decomposition of thiourea in water solutions. The respective samples of these materials were heated with water at 100°C. for two hours and then tested for ammonium thiocyanate. It was found that the thiourea sample showed an absence of ammonium thiocyanate, indicating that under these conditions no conversion had taken place.

TABLE 1

Solubility of thiourea (recrystallized from water) in water

THIOUREA	SOLVENT	THIOUREA	THIOUREA	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C*
0 2968	2 9993	9 0	0 0229	12 43
0 4050	2 9543	12 06	0 0314	19 88
0 5113	2 9899	14 60	0 0389	25 11
0 6369	2 9550	17 73	0 0486	30 38
0 7855	2 9862	20 83	0 0586	35 23
1 2715	1 9846	39 05	0 1317	57 05
0 9010	3 0165	23 00	0 0658	38 31
1 1094	2 8897	27 74	0 0833	44 30
1 2975	2 9727	30 38	0 0937	47 34
1 0700	1 9636	35 27	0 1143	53 02
1 5590	1 9423	44 53	0 1598	62 85
1 8848	1 9927	48 61	0 1829	67 43
1 9197	1 5217	55 78	0 2299	75 96
2 2502	1 5084	59 87	0 2610	81 28

EXPERIMENTAL RESULTS

The results of the various thiourea solubility determinations are presented in tables 1 and 2. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data were plotted on a large scale according to the method of Hildebrand and Jenks (5), as the log N_2 versus 1000/T. The solubilities at rounded temperatures were read off and are given in table 3.

TABLE 2

Solubility of thiourea (recrystallized from water and methanol)

THIOUREA	SOLVENT	THIOUREA	THIOUREA	SOLUBILITY TEMPERATURE
		Solubility in water		
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C*
0 5199	2 9260	15 09	0 0404	25 90
0 4905	2 7676	15 05	0 0402	26 02
0 9347	2 6717	25 92	0 0766	42 00
1 0462	2 8386	26 93	0 0800	43 11
1 9521	1 9358	50 21	0 1925	69 26
		Solubility in methanol		
0 2101	1 5484	11 95	0 0540	25 11
0 3108	1 5879	16 37	0 0760	40 80
0 4064	1 5409	22 01	0 0999	53 76
0 5046	1 5500	24 56	0 1205	62 00
		Solubility in ethanol		
0 0864	2 3103	3 61	0 0221	20 25
0 1107	2 2510	4 69	0 0289	31 99
0 0873	1 5303	5 40	0 0334	37 69
0 1426	2 1111	6 33	0 0393	45 14
0 1465	1 8861	7 21	0 0449	51 22
0 2135	2 3031	8 48	0 0531	58 05
0 2457	2 2585	9 81	0 0618	64 77

TABLE 3

Solubility of thiourea in water and alcohols at rounded temperatures

(Expressed in mol fractions of thiourea)

TEMPERATURE	WATER	METHANOL	ETHANOL
degrees C			
20	0 0314	0 0481	0 0220
25	0 0389	0 0539	0 0247
30	0 0478	0 0603	0 0277
35	0 0583	0 0673	0 0312
40	0 0707	0 0748	0 0349
45	0 0856	0 0833	0 0392
50	0 1023	0 0922	0 0438
55	0 1221	0 1025	0 0492
60	0 1450	0 1150	0 0554
65	0 1700	0 1292	0 0622
70	0 1968	0 1452	0 0701
75	0 2243		
80	0 2533		
85	0 2860		

DISCUSSION OF RESULTS

The results of the solubility determinations in water were compared with those published by earlier workers. Dehn (4), some years ago, made a single qualitative determination of the solubility of thiourea in water at a temperature of 20°C. to 25°C. This result, as the author states, is not of a high degree of accuracy. Kettner (8) somewhat later determined the solubility of thiourea in water over a temperature range of 0°C. to 145°C. His determinations were made at 0°, 50°, 56.5°, 97.2°, 120.6°, and 145°C. Hence, comparison with the author's data could be made at two points only, viz., 50°C. and 56.5°C. These determinations show some variance from the results obtained in the present research, especially the value at 50°C. Oliveri-Mandala (11, 12) more recently determined the solubility of thiourea in water at temperatures from 10°C. to 25°C. The results at 20°C. and 25°C. when compared to the present research show considerable variation, especially the value at 25°C. The results of the above-mentioned investigators are compared in graphic form with the author's work in figure 1, where the data are plotted according to the method of Hildebrand and Jenks (5). Over a temperature range of 20°C. to 60°C., it is found that a straight line results; above 60°C. departure from the straight-line function increases and becomes greatest at the higher temperatures.

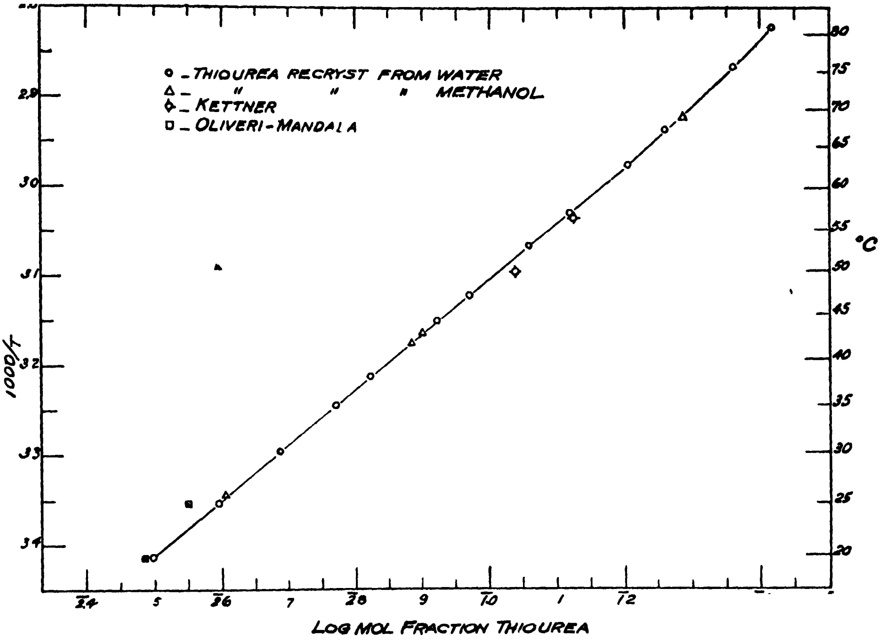

FIG. 1. SOLUBILITY OF THIOUREA IN WATER

Data for a sample of thiourea recrystallized from water and methanol are also presented. Here it is observed that the solubility determinations coincide with those already determined on the sample recrystallized from water only. It is thus apparent that the solubility of thiourea was not affected by the nature of the solvent from which it was recrystallized. A study of tables 1 and 2 shows the deviation obtained relative to the solubility of thiourea on the two samples used, viz., that recrystallized from water and that recrystallized from water and methanol. The fact that the results on the solubility determinations of the two samples of thiourea show such close agreement leads to the conclusion that these determinations are more accurate than those of previous published work.

It is felt that the foregoing results are accurate to well within ± 0.1°C. of the true solubility temperature. This figure represents the maximum deviation, whereas some of the determinations deviate much less. Between the temperature of 20°C. to 60°C., where the straight-line function exists, the mean deviation in solubility temperature for both samples of thiourea used was 0.07°C. It is believed that the solubility results obtained with both samples are of the same degree of accuracy. For that reason no distinction in the final results is made. The values of the solubility of the respective samples of thiourea were read off from the large plot previously referred to. From this plot the equation of the straight line was determined, and found to be $\log_{10} N = -1621.6 \ (1/T) + 4.029$. This is valid over the temperature range 20°C. to 60°C. It gives results to within one part per thousand of the values obtained from the plot.

The fact that the $\log N$ versus $1/T$ curve is a stright line over the temperature range of 20°C. to 60°C. leads one to inquire whether or not ideal solutions are encountered in this range of temperature. To attempt to extrapolate $\log N = 0$ is difficult, because it is known that above 60°C. the solubility of thiourea departs from a straight-line function, with increasing rapidity as the temperature is elevated. However when Kettner's (8) data at higher temperatures are plotted with those of the author, a smooth curve results and on extrapolation the curve almost intersects at the absolute melting point, i.e., where $\log N = 0$. The shape of the curve indicates that a reverse S form of curve discussed by Mortimer (10) is not formed. No data seems to be available concerning the latent heat and fusion of thiourea (no doubt because of the molecular transformation at its melting point). Hence, a comparison of the experimental and ideal shape of the line was not possible. It may be said that when the slope, 1621.6 (assumed to be constant over the entire range, which is not true to the fact) is multiplied by 4.583, a value of approximately 7400 calories is obtained. If the solution were ideal, this value would represent the latent mol heat of fusion of thiourea.

To determine further whether or not ideal solutions were formed by thiourea in water, a search for vapor pressure data was made. Apparently no data on the vapor pressure of thiourea in water solutions is available. Hence no comparison or calculation can be made to determine whether or not deviation from Raoult's law exists.

The solubility results of thiourea in methanol and in ethanol are found in table 2. These results are also presented in graphic form in figure 2. It is observed that between the temperature range of 20°C. to 70°C., thiourea in methanol and ethanol does not form a straight line when plotted according to the method of Hildebrand and Jenks (5). One would expect from the nature and chemical constitution of thiourea that it would be readily soluble in water, less soluble in methanol, and least soluble in ethanol. However, this is not the case. An unexpected phenomenon occurs, as shown in figure 2. The curves of the solubility of thiourea in water and methanol cross at about 43°C., i.e., at temperatures below 43°C. thiourea is more soluble in methanol than in water, and at temperatures above that point is more soluble in water than in methanol, when expressed on the mol fraction basis. The exact point where thiourea in methanol crosses the thiourea and water curve is where the mol fraction is equal to 0.08017, which is equivalent to a temperature of 43.24°C.

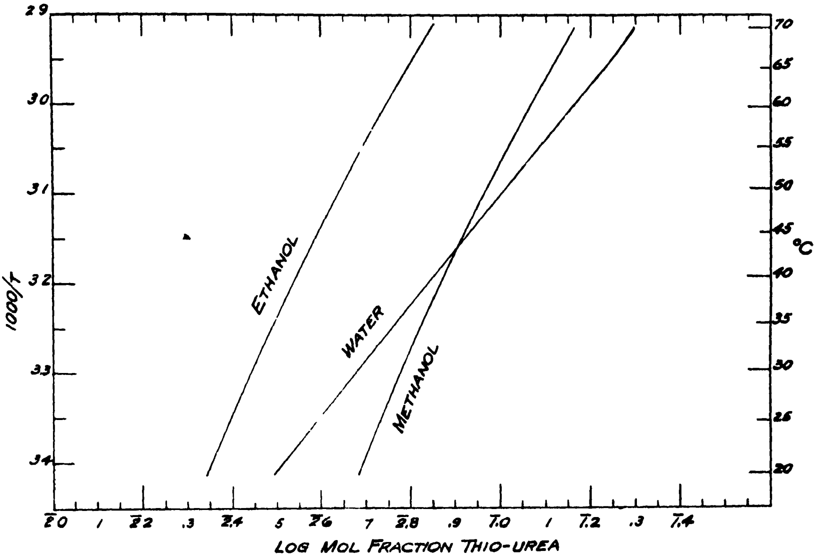

FIG. 2. SOLUBILITY OF THIOUREA IN WATER, IN METHANOL, AND IN ETHANOL

The solubility of thiourea in ethanol is as would be expected, viz., less than in water or methanol. No previous determinations on the solubility of thiourea in water, in methanol, or in ethanol over the temperature range studied have been made.

SUMMARY

1. Two samples of thiourea have been carefully purified and analyzed.

2. Nineteen determinations of the solubility of thiourea in water have been made, using the synthetic method in the temperature interval 15°C. to 80°C.; the precision in these runs is much higher than any previously published. The data may be accurately represented by the equation

$$\log_{10} N = -1621.6\ (1/T) + 4.029$$

in the temperature interval 20°C. to 60°C.

3. The solubility of thiourea in methanol and ethanol has been determined by the synthetic method from 20°C. to 70°C.

The author wishes to express his gratitude to Prof. A. A. Sunier for his interest and advice during the progress of this work, and to the Rochester Gas and Electric Corporation for the use of their equipment.

REFERENCES

(1) Alexejew: Wied. Ann. **28**, 305 (1886).
(2) Assoc. Official Agr. Chem., Methods of Analysis, p. 8 (1925).
(3) Assoc. Official Agr. Chem., Methods of Analysis (Modification of Total Sulfur Method), p. 68 (1925).
(4) Dehn: J. Am. Chem. Soc. **39**, 1400 (1917).
(5) Hildebrand and Jenks: J. Am. Chem. Soc. **42**, 2180 (1920).
(6) International Critical Tables, Vol. I, p. 177. McGraw-Hill Book Co., New York (1926).
(7) Lunge: Coal Tar and Ammonia, Vol. III, p. 1310, 5th ed. D. Van Nostrand Co., New York (1916).
(8) Kettner: Dissertation, Amsterdam, 1919.
(9) Merriman: J. Chem. Soc. **103**, 629 (1913).
(10) Mortimer: J. Am. Chem. Soc. **44**, 1416 (1922); **45**, 633 (1923).
(11) Oliveri-Mandala, E.: Gazz. chim. ital. **56**, 889 (1926).
(12) Oliveri-Mandala, E.: Gazz. chim. ital. **60**, 872 (1930).
(13) Pfeiffer: In Lunge and Berl's Techn. Chem. Unt. Meth. **3**, 373, 6th ed.
(14) Reynolds and Werner: J. Chem. Soc. **83**, 1 (1903).
(15) Seidell: Solubilities of Inorganic and Organic Substances. D. Van Nostrand Co., New York (1919).
(16) Shnidman and Sunier: J. Phys. Chem. **36**, 1232 (1932).
(17) Sunier: J. Phys. Chem. **34**, 2582 (1930).
(18) Sunier and Rosenblum: J. Phys. Chem. **32**, 1049 (1928).
(19) Treadwell-Hall: Analytical Chemistry, Vol. II, p. 340, 5th ed.
(20) Ward: J. Phys. Chem. **30**, 1316 (1926).
(21) Werner: J. Chem. Soc. **99**, 2166 (1912).

ON THE EBULLIOSCOPIC METHOD FOR DETERMINING THE EQUILIBRIUM CONSTANT OF ESTERIFICATION

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A method of determining the so-called equilibrium constant of esterification by ebullioscopic measurements has previously been described (1). In the present investigation, a new ebullioscopic apparatus was used and some improvements and simplifications introduced in the technique.

It is clear that the boiling points of two reacting mixtures, the first one containing say 1 mole of ethyl alcohol and 1 mole of acetic acid, and the other 1 mole of ethyl acetate and 1 mole of water, differ considerably at the beginning of the reaction. The boiling temperatures, however, approach each other as the mixtures tend towards the equilibrium state. We may consider that equilibrium is established when the two mixtures boil at the same temperature. The composition of the two mixtures which must be identical is determined in order to calculate the equilibrium constant.

Previous experiments, with mixtures of the reacting substances in molar proportions, showed that it was not easy to get identical values for the boiling points of the two mixtures undergoing changes in opposite directions. Jozefowicz obtained a difference of 0.1°C., whilst Miss Blaszkowska succeeded in reducing the difference to 0.04°C. In the latter case the boiling point of the equilibrium mixture could be extrapolated with an approximation of 0.010°C. These relatively small differences could be due either to errors in the ebullioscopic measurements or to the very small velocity of reaction in the neighborhood of the equilibrium state.

The exact determination of the boiling point of a mixture containing volatile liquids is complicated by the fact that the volatile parts of the mixture evaporate and accumulate in the dead space of the ebullioscopic apparatus; this may cause differences in the measurements. On the other hand, the velocity of reaction may decrease to such a degree that the equilibrium and the equalization of the boiling points of the two mixtures might perhaps never be reached in practice. In order to investigate the cause of the phenomenon, the conditions governing ebullioscopic measurements have been improved. A new ebullioscopic apparatus suitable for investigating mixtures of volatile substances (2) and provided with a stopcock in order to determine the correction for the dead space of the apparatus has been constructed. The new apparatus is shown in figure 1. The test tube sealed to the part B is immersed in the boiling liquid. This test tube is filled with mercury, into which the bulb of the thermometer dips. The temperature read on the thermometer does not correspond to the true boiling point on account of the overheating of the liquid, a correction for which can, however, be introduced without difficulty (3). In measurements of boiling points it is very important to obtain in both pieces of ebullioscopic apparatus an equal intensity of boiling. For this purpose they are provided with drop-counters, *f*. The intensity of the heating is regulated in such a manner that the number of drops flowing from the condenser D through the tube F is equal for both mixtures, reacting in opposite directions.

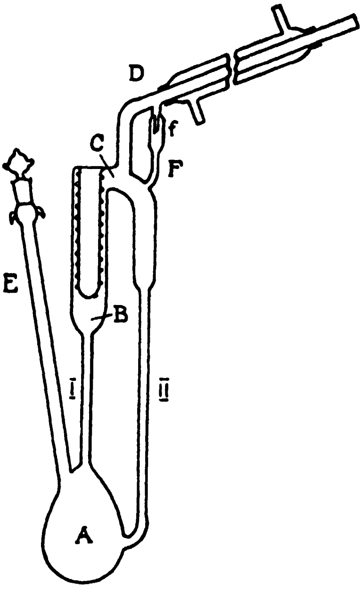

FIG. 1

ESTABLISHMENT OF THE EQUILIBRIUM AND DETERMINATION OF THE BOILING POINTS

The arrangement of the apparatus is shown in figure 2. The two ebullioscopes, A and B, each filled with one of the two mixtures undergoing changes in opposite directions, are connected by means of stop-cocks 1 and 2 with a manostat E of 3 to 4 liters capacity. The stop-cock 5 allows us either to fill the apparatus with nitrogen or to connect it with the atmosphere.

During the first part of the experiment (lasting several weeks) two other ebullioscopes, C and D, remain empty and the stop-cocks 3 and 4 are closed. The experiment is started by filling the whole apparatus with nitrogen. Then A and B are filled with the two mixtures. The stop-cock 5 is then closed and the bulbs of both ebullioscopes heated until the liquids begin to boil. The stop-cocks 1 and 2 are then opened. After having established a rate of equal boiling, measurements of the boiling points of the mixtures are started. For this purpose only one thermometer with an arbitrary scale is used, and it is carried over several times from one test tube to the other in order to eliminate the influence of the pressure changes in the whole apparatus. After measuring the difference of the boiling points, $\Delta t = t_A - t_B$, the stop-cocks 1 and 2 are closed and the boiling of the mixtures maintained for several days. The measurement is repeated by opening each time the stop-cocks 1 and 2. When, for example, the formation of ethyl acetate is investigated, it is possible to fill the ebullioscopes with mixtures which are quite near to the equilibrium state, for instance, which differ in their boiling points by not more than 0.300°C., or even 0.060°C. The realization of practically identical boiling points for both liquids, within 0.001°–0.003°C., requires four to nine weeks. In some cases, when impurities were probably present or when the one-sided evaporation produced a little difference in the composition of the two liquids, we noted a greater difference. As is shown in the table, Δt did not, however, exceed 0.010°C.

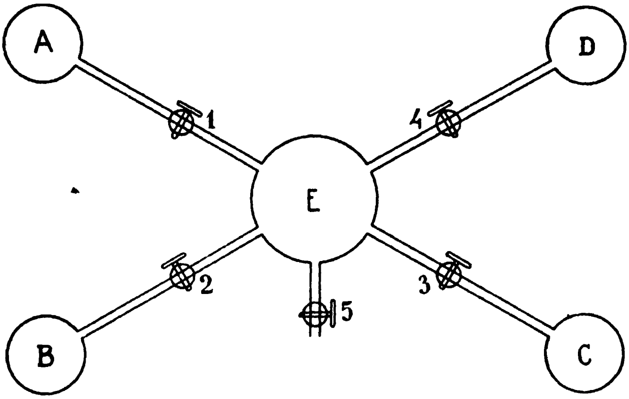

FIG. 2

DETERMINATION OF THE COMPOSITION CORRESPONDING TO THE EQUILIBRIUM STATE

In the previous work the composition of the liquid in a state of equilibrium was determined by considering the function:

$$t = f(K')$$

where t is the boiling point of the mixture at the pressure of 1 atmosphere and

$$K' = \frac{c_3'c_4'}{c_1'c_2'}$$

c_1', c_2', c_3', c_4' being the concentrations of the acid, alcohol, water, and ester respectively. On plotting the values of K' against t a curve is obtained which allows us to find the equilibrium constant $K = \frac{c_3c_4}{c_1c_2}$, when the boiling point, t_C, of the equilibrium mixture is known, or may be determined by extrapolation. In the present investigation the method of determining the constant K or the concentrations, c_1, c_2, c_3, c_4, corresponding to the equilibrium state, has been considerably improved and simplified. It consists in the following operations. When the equalization of the boiling points of the two mixtures is reached, a mixture M is prepared, which is very near to the equilibrium state, but still contains a small excess of water and ester. This mixture is introduced into the third ebullioscope C. Subsequently a corresponding mixture of acid and alcohol, N, is prepared and introduced into a bath at 0°C. Then the bulbs of the three ebullioscopes, A, B, and C, are heated and the boiling points t_A, t_B and t_C determined by means of the same thermometer. The liquids boil under some unknown pressure p'. Let the boiling temperatures be unequal, say $t_A > t_B > t'_C$. As mentioned above, the difference, $t_A - t_B$, is small and does not exceed 0.010°C. Now the stop-cock 3 is closed, the bulb of the apparatus C cooled and a small quantity of the liquid N, containing alcohol and acid, is introduced. The measurements are repeated by reading again the temperatures in A, B, and C. After repeating this procedure several times, a mixture is finally obtained which has a boiling temerature t_C fulfilling the condition: $t_A > t_C > t_B$. In order to obtain a complete series of data, it is necessary once more to add the same quantity of the mixture N containing acid and alcohol, and to find that the boiling point of the liquid in C is now higher than that of two others, say $t''_C > t_A > t_B$. With all these data the composition of the equilibrium mixture may be obtained without any difficulty.

When the boiling point of the mixture in equilibrium is known, a fourth ebullioscope, D, filled with water is used. After opening the stop-cocks 3 and 4 the boiling temperatures t_C and t_D are measured under the pressure existing in the system. Then a manometer filled with water is connected through the stop-cock 5 and a series of determinations of the boiling points of water (t_D) and of the liquid (t_C) at different pressures is carried out, in order to determine the value of $\frac{dt}{dp}$ for this liquid and obtain from it by calculation the boiling point at 760 mm. of mercury.

Up to the present, we have carried out several investigations only on the reaction that takes place in the formation of ethyl acetate. It is quite clear, however, that the same method may be applied in many other cases.

EXPERIMENTAL DATA

Three series of experiments were made in order to test the application of the method described. The reacting substances were carefully purified by methods described in previous papers and the mixtures weighed out by means of the apparatus previously described (4).

TABLE 1

EXPERIMENTAL VALUES	I	II	III
1. Proportion of alcohol and acid	1:1	3:1	1:3
2. Initial temperature difference Δt_0	0 061°C	0 233°C.	0 605°C.
3. Time in days	25	42	44
4. Final temperature difference, Δt	0 000°C.	0 002°C.	0 008°C.
5. Number of drops, n .	120	108	109
6. Correction for the dead space	−0 018°C.	−0 014°C.	−0 048°C.
7. Correction for overheating .	−0 033°C	−0 034°C.	−0 034°C.
8. Boiling point corresponding to the equilibrium state ..	76 25°C.	73 66°C.	90 78°C.
9. Equilibrium constant, K	3 82	2 47	4 74

TABLE 2

Changes in $t_A - t_B$ *with time*

3 moles alcohol and 1 mole acetic acid

TIME	CHANGES IN $t_A - t_B$	TIME	CHANGES IN $t_A - t_B$
days		*days*	
0	0 340	43	0 023
2	0 320	54	0 009
5	0 290	64	0 003
14	0 182	65	0 002
24	0 087	66	0 001

In table 1 the following data are given: (1) the proportion of ethyl alcohol and acetic acid in the "initial" mixture; (2) the initial temperature difference, Δt_0; (3) the time of duration of measurements, in days; (4) the final temperature difference, Δt, when the equilibrium state was taken as "established"; (5) the number of drops, n, flowing through the drop-counter per minute; (6) the correction for the dead space of the ebullioscope; (7) the correction for the overheating of the liquid; (8) the boiling point of the liquid in equilibrium at 1 atmosphere (compared with the boiling point of water as the standard substance); (9) the equilibrium constant *K*. The experiments were made by Sobolewski (column I), Kwiecinska (column II), and Bochenk (column III).

Table 2 illustrates the changes in the difference $t_A - t_B$ with time. It is a repetition of experiment II and was carried out by Dobry-Szapiro.

It seems that this difference, after several transports of the thermometer from one apparatus to the other, may be established with an accuracy of 0.001° – 0.002°C. It is very probable that this accuracy is greater than that in the determination of the boiling point of the reacting liquid in the pure state. The method thus allows of more accuracy than the method of preparation of the pure liquid substances, and the figures in table 4 should be considered to apply to the substances used in our experiments. In two experiments where different samples of reacting substances were used, the mixture when in the equilibrium state gave a difference between the boiling points equal to 0.017°C., whereas the differences $t_A - t_B$ observed for the two mixtures in one experiment did not exceed 0.002°C. Table 3 gives an example of the method for determining the composition of the equilibrium mixture, C, and its boiling point.

TABLE 3

ALCOHOL	ACID	ESTER	WATER	$K = \frac{c_3c_4}{c_1c_2}$	Δt
					degrees C.
0 9242	0 0404	0 4018	0 4018	4 321	0 202
0 9233	0 0389	0 4033	0 4033	4 529	0 091
0 9225	0 0381	0 4041	0 4041	4 646	0 027
0 9221	0 0377	0 4045	0 4045	4 707	0 010
0 9218	0 0374	0 4048	0 4048	4 753	0 003

TABLE 4

Values of K obtained by Swietoslawski and by others

MOLE ALCOHOL / MOLE ACID	*K*			
	Ebullioscopic method	Poznanski	Blaszkowska	Tobbin
1:1	3 82	3 79	3 76	3 70
3:1	2 47	2 45	—	—
1:3	4 74	4 72	—	—

The calculation of *K* can be performed with great accuracy. In table 4 we have given for *K* only two decimals because we consider that the methods of purification of the reacting substances are not sufficiently trustworthy to guarantee the third decimal. In table 4 is given a comparison of the data obtained by us and by other authors (5).

SUMMARY

The ebullioscopic method for determining the composition of equilibrium mixtures seems to be very accurate and is applicable in all cases where the boiling temperature of the equilibrium solution differs considerably from the boiling points of the initial mixtures of reacting substances The preparation of the equilibrium mixtures, when the equilibrium has been established, may be performed with a high degree of accuracy In the case of the formation of ethyl acetate the ebullioscopic method is even more trustworthy than the methods of purification of the reacting substances. The values for the equilibrium constant of esterification in the liquid phase have been found for mixtures whose initial composition was 1 mole ethyl alcohol: 1 mole acid, 3 moles alcohol· 1 mole acid, and 1 mole alcohol: 3 moles acid The boiling points of the corresponding equilibrium mixtures were found to be. 76 25°C , 73 66°C , and 90 78°C , respectively.

REFERENCES

(1) Swietoslawski, W , Blaszkowska, Miss Z , and Josefowicz Bull acad sci. Polonaise **1929**, 149
(2) Swietoslawski, W Anales soc españ fís quím **27**, 439 (1929)
(3) Swietoslawski, W Bull acad sci Polonaise **1929**, 464–5
(4) Blaskowska, Z Ind Eng Chem , Anal Ed **1**, 170 (1929)
(5) Poznanski, S Roczniki Chem **8**, 387 (1928)

PHOTOVOLTAIC EFFECTS IN GRIGNARD SOLUTIONS. III

New Observations. A Possible Theory

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This article[1] records certain new observations on photovoltaic effects in Grignard solutions and in other substances, and outlines briefly certain theoretical considerations which may apply to the effect. The work is a continuation of that described in previous papers by the writer (1).

NEW OBSERVATIONS

The results here reported are summarized from observations on about eighty cells, some of which, because of changes of electrodes or other experimental conditions, are equivalent to several single cells each. About sixty of the cells contained Grignard solutions, and about twenty were cells of other types which it was desired to study for purposes of comparison. In all, results are now available from more than three hundred cells, on which the total number of readings would probably exceed two hundred thousand.

The tests with the device for circulating the solutions, described in the previous paper (1), have been continued; so far, they seem to confirm the conclusions stated there. The writer wishes to make further experiments before stating final conclusions, the question whether two effects exist is still open, though the conclusion seems very probable.

For work in this field, it would be very convenient if some electrode could be found which would be entirely free from any response to light, when immersed in Grignard solutions. So far, no substance has been found which does not give some small photovoltaic effect in these solutions. Mercury covered with carefully dried calomel, in ethylmagnesium bromide solution, gives only a few millivolts; probably the calomel protects the mercury surface from the light, or from the products formed by the light. But even this small response is thirty to forty times the error of measurement. And with phenylmagnesium bromide, the solution becomes discolored. Hence this type of electrode, while perhaps the most nearly inactive so far found, is far from satisfactory. It is therefore necessary in studying the responses of single electrodes to use H-shaped cells in which the electrode in one arm can be kept completely dark. While these cells give satisfactory results, they require the use of larger volumes of solution than would otherwise be necessary. The use of standard reference electrodes, such as the calomel half-cell, has not been attempted, because of the diffiulty in bridging over from aqueous solutions to ether solutions which must remain absolutely anhydrous, and because of the uncertainty concerning the electromotive forces that might be introduced at the liquid junctions. A really inactive electrode would be very convenient.

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[1] Abstracted from a thesis presented to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1931.

The failure of phenylmagnesium bromide solutions to transport any considerable amount of effect of illumination with it in the circulation experiments seems to indicate that the effect in this case may be due to some kind of sensitive film formed on the electrode surface. The capacitance measurements made by Hammond (2) seem to make it clear that thin films always exist on the electrode surfaces in these cells. Tests reported in the preceding article (1) indicated that the response with platinum electrodes in Grignard solutions is not due to adsorbed oxygen; electrodes held at 800°C. in a hydrogen atmosphere for some hours, and cooled in hydrogen, behaved the same as electrodes flamed and cooled in air, or electrodes kept between slices of sodium in ether. These precautions seem sufficient to exclude the possibility of effects due to oxygen, which might have been expected to produce some effect if present in or on the electrodes, where it could react under the stimulation of light. Electrodes cooled in nitrogen behave similarly. It seems probable, therefore, that the regularly observed effects are not due to films of gas on the electrodes.

However, it seems very clear that other kinds of film on the surface of a platinum electrode can affect its response to light. For example, a film of the oxidation product formed by the momentary exposure of an electrode wet with Grignard solution to the air, or the film formed by dipping a moist electrode into a Grignard solution, will change the behavior of a platinum electrode, as shown in figure 1. These films raise the dark voltage to unusually high values, sometimes more than one volt, and they increase the resistance of the cells enormously. As the figure shows, the response to light may be even greater than without the film. Exact values of the thickness of these films cannot be given, but the order of magnitude is about 0.1 to 0.01 mm.

Preliminary results on several other metals in Grignard solutions are available. With lead electrodes, the presence of a surface layer of oxide seems to make no important difference in the response. With aluminum, the response is slightly larger if the layer of oxide is left on the surface, as the sheet comes from stock, than if the sheet is freshly polished just before inserting it in the solution. Clean copper surfaces show a good response.

Surface layers of oxide give rise to differences in the response which are undoubtedly due to the light-sensitiveness of the cuprous oxide itself. The response of cuprous oxide in the solutions mentioned is less than in some aqueous solutions that have been studied.

The curve in figure 2 was obtained from a type of cell obtainable commercially, which contains a sensitive electrode of cuprous oxide on copper, an inert electrode of lead, and a solution of lead acetate or nitrate. The curve was obtained with potentiometric equipment, so that the cell supplied no current except the minute amounts used in obtaining balance. Used with a milliammeter, the response and recovery of the cell are even more rapid—too rapid for an instrument to follow. The current changes from zero in the dark to several milliamperes in intense light. The tendency to reach a

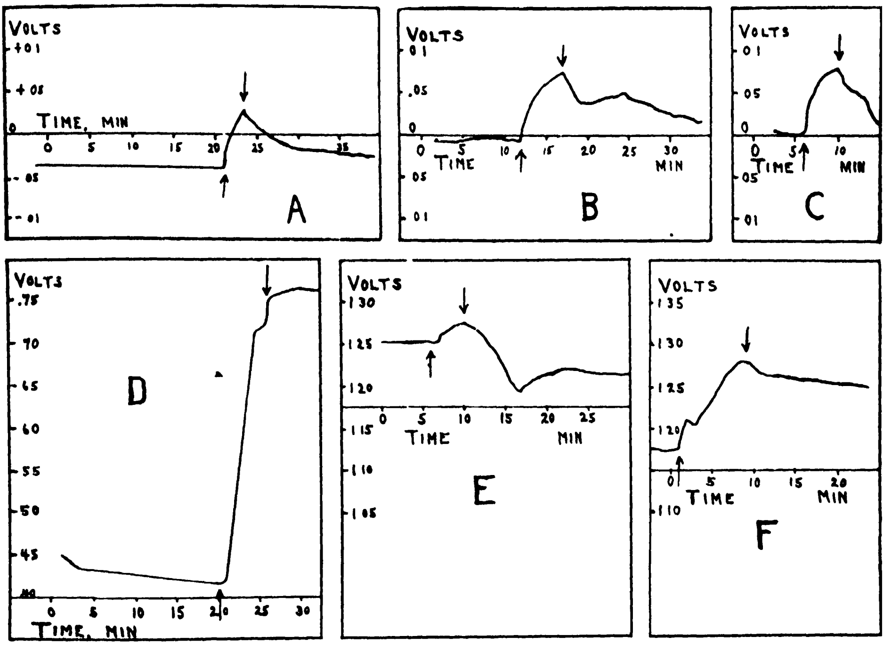

FIG. 1. CELL NO 101, Pt | C_6H_5MgBr | Pt, WITH ONE PLATINUM ELECTRODE ILLUMINATED

Curve A is for a clean bright platinum electrode; curves B and C are for another similar electrode, but taken on different days. Curve D is for the electrode of curve A after it was coated with the oxidation products from the Grignard reagent; curves E and F are for other coated electrodes coated with hydrolysis products of the Grignard reagents.

The upward-pointing arrows indicate the time at which illumination begins; the downward-pointing arrows indicate the end of the illumination.

maximum response quickly, and then to show a decreasing response with continued illumination, seems to be usual in cuprous oxide.

Cells with sodium and potassium electrodes in Grignard solutions have been given some study. The metals were cut and handled under anhydrous ether, except that they were kept in a nitrogen atmosphere while they were transferred to the solutions. The surfaces, bright when first cut, become bluish gray on standing. This change of color probably indicates formation of some kind of surface film on the electrodes; but it is doubtful if the films contain oxygen, or if they do, whether these metals would release

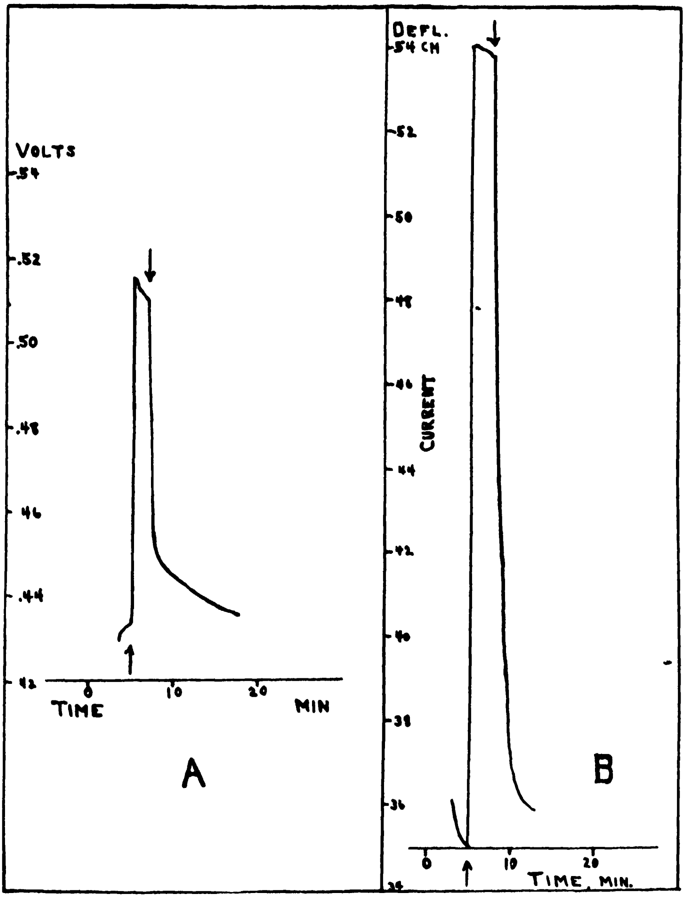

FIG. 2. CELL NO 401, A COMMERCIAL TYPE OF PHOTOVOLTAIC CELL, Cu | Cu_2O | $PbC_2H_3O_2$ | Pb

Curve A shows the voltage response, curve B the current-response, to white light. This type of cell gives larger responses than the types referred to in figure 5.

it under illumination. The sodium electrodes gave small but remarkably consistent responses both to light and to x-rays. Typical curves are shown in figure 3. The potassium gave smaller and more erratic responses; on standing a few days, the metal dissolved completely, and was replaced by a dark fibrous mass, probably magnesium deposited electrolytically by local action. This reaction deserves further study.

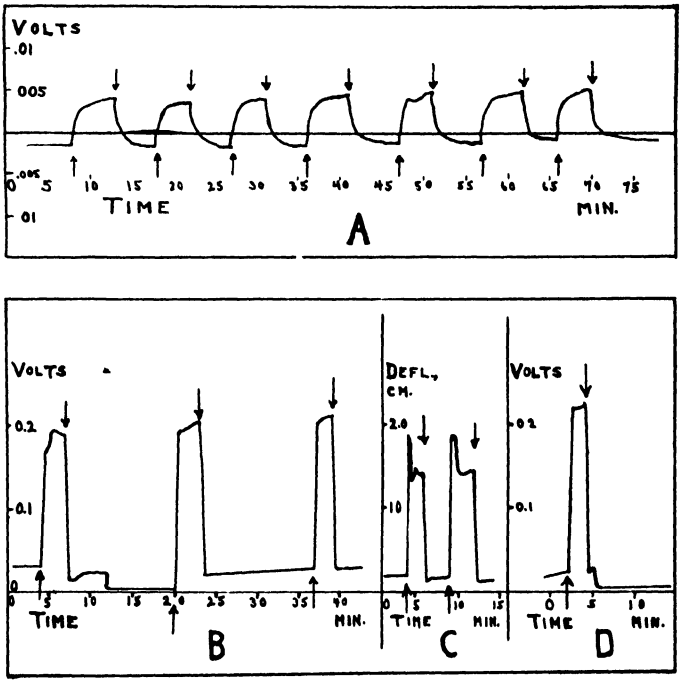

Fig. 3. Cell No. 105, Na | C_2H_5MgBr | Na, One Electrode Illuminated

Curve A shows the response to white light, the results being unusually reproducible. Curve B shows the voltage response of this cell to x-rays; curve C the current-response to x-rays; and curve D shows another voltage response curve taken just after the current curves were obtained, showing that polarization by the current did not affect the reproducibility of the voltage responses.

Somewhat similar cases of formation of sensitive films in aqueous solutions are known. Grube and Baumeister (3) and others have studied the light-sensitivity of anodically polarized platinum electrodes. The response is of the type that shows a reversal on continued illumination. On the other hand, the writer found that anodically polarized aluminum in aqueous solutions is relatively insensitive both to visible light and to x-rays. Ultraviolet light gives a small but consistent effect.

The general conclusion from these observations seems to be that while surface layers do not necessarily cause photovoltaic effects to appear, they do modify the effect frequently, and may in some cases be responsible for the appearance of the effect. The experiments described above seem to indicate that the effect is not due to oxygen in all cases. The study of such surface effects seems to the writer to be well worth continuing, since it seems probable that the results can be of great help in deciding the nature of photovoltaic action. The study of the effects of depolarizers, described briefly in the preceding article, seems equally promising, and is being continued.

A number of cells have been made in which Grignard solutions were hermetically sealed in glass. These cells have shown a good response to light after three years; under proper conditions, therefore, their useful life is considerable.

In collaboration with Dr. H. E. Hammond, the writer has studied the response of a number of Grignard cells to x-rays. In general, the responses obtained have been large compared with those from visible light; a typical case is shown in figure 4. They seem to obey the same logarithmic law as applies to other cases of the photovoltaic effect, though the law is only a very rough approximation. These observations were made under conditions in which the shielding of the circuits was not entirely satisfactory, so that there is some possibility that electromagnetic induction, together with rectifying properties of the cells, could give rise to a spurious effect. While auxiliary experiments made at the time seemed to prove that such spurious effects were negligible, there were discrepancies in the behavior of certain cells which did not seem explainable otherwise. The results are therefore regarded as preliminary, and are communicated with due reservation. More satisfactory apparatus has been prepared, and additional work is to be carried out with it. The effect gives some promise as a method of measuring x-ray intensities.

It is interesting to compare with the preceding results the curves obtained from photovoltaic cells which contain no electrolyte. The light-sensitive substance was either cuprous oxide or selenium, though other substances are known which give the effect. Such cells can be made by forming a layer of cuprous oxide on copper by heating (such plates are used commercially in the cuprous oxide type of rectifiers which have come on the market recently), and then pressing a layer of wire cloth against the oxide, or plating or sputtering a metal layer on it. When illuminated through the wire cloth, current tends to flow, the wire cloth becoming positive by several hundredths of a volt. While some investigators have regarded this phenomenon as a photoelectric effect, the writer has included it with the photovoltaic effects, since it is essentially the production of an electromotive force by light, and since the response not only follows the same roughly logarithmic law as other photovoltaic effects, but shows the same tendency to diminish and even to reverse its direction under prolonged intense illumination. Typical curves are shown in figure 5. Copper and nickel wire cloths have been used, the nickel giving a somewhat larger response. The response and recovery are very rapid in these cells, so that they can follow fluctuations in the illumination up to frequencies of 1000 per second, beyond which the response becomes small. Their dark voltage is usually zero. The reversal of the response is shown in the last two illuminations in figure 5. The recovery from such a reversed response is direct; positive values are not retraced. Subsequent responses are reversed. It is not known how long such a negative response would continue; the cell which gave the curve reproduced here had completely recovered its normal charac-

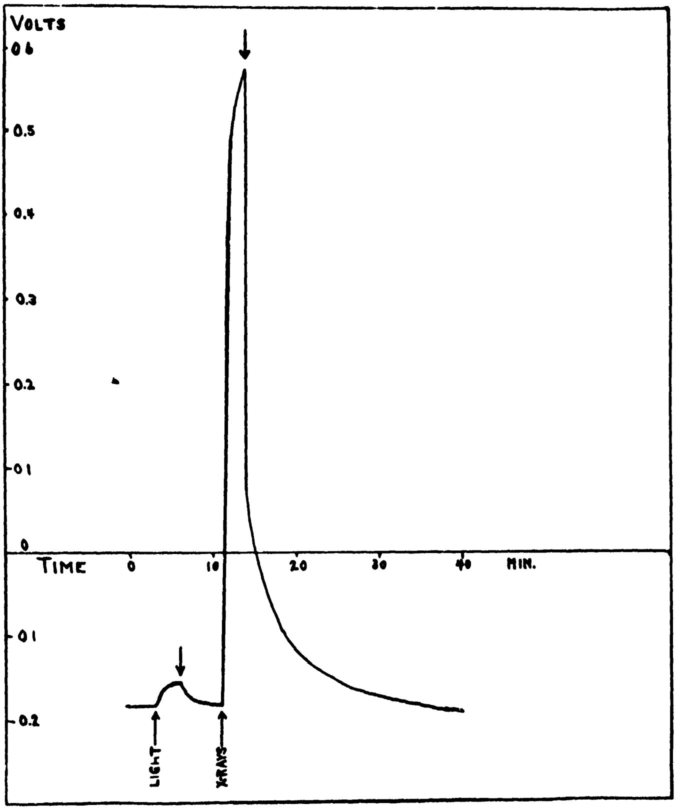

Fig. 4. Cell No. 107, Pt | C_6H_5MgBr | Pb, Platinum Electrode Illuminated

The curve compares the voltage response to intense white light with that obtained from x-rays. The latter effect is being reinvestigated.

teristics by the following morning. The reversal seems to occur equally quickly whether the cell delivers maximum current or none. Substances which behave in this respect like cuprous oxide, generally show a reduction in electrical resistance on illumination. They also show a certain amount

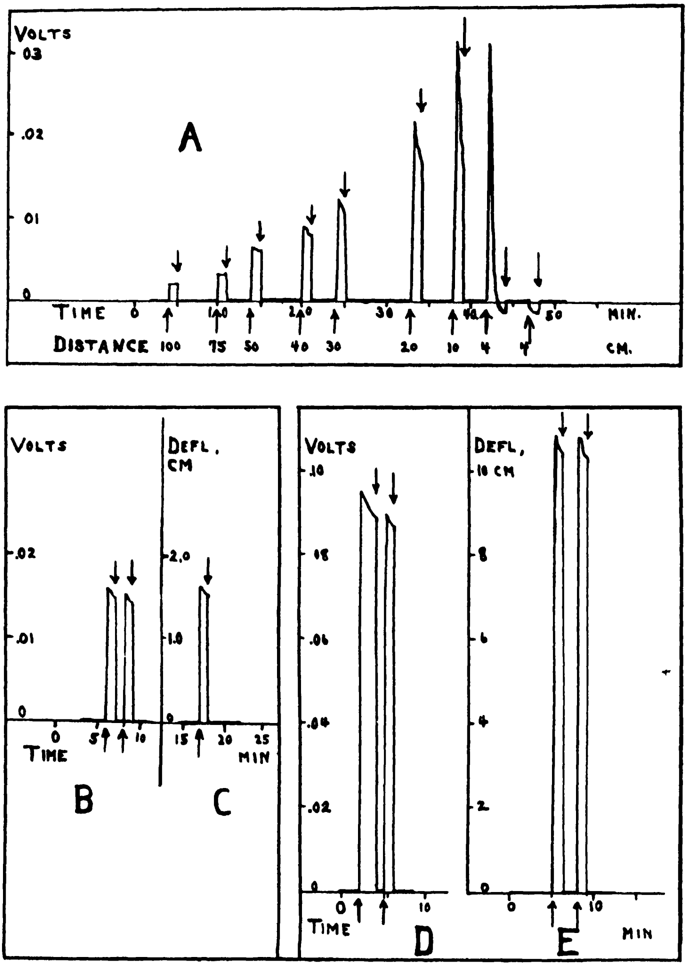

FIG. 5

Curve A shows the voltage response to white light of different intensities, of Cell No. 400, Cu | Cu_2O | Cu, a "dry" cell with the outer coating of copper electroplated on the Cu_2O. The reversal of the voltage response on intense illumination is noteworthy. Curves B and C compare the voltage and current responses of Cell No. 405, a dry Cu | Cu_2O | Cu cell in which the outer electrode was a copper wire cloth pressed against the cuprous oxide, with the similar responses in curves D and E for Cell No. 404, a Ni | Cu_2O | Cu cell with the copper wire cloth replaced by one of nickel.

of unilateral conductivity, which permits their use in rectifiers. Some writers have claimed that the rectifying ability and the photovoltaic responses are directly proportional to each other, but this statement is disputed by others.

The striking similarity of the behavior of these dry cells to that of electrolytic cells raises the question whether the effect in the dry cells can be due to traces of moisture. Apparently the answer to this question is negative. One such cell was kept heated to above 100°C. for some time, then was cooled in a desiccator in which it was kept for several weeks. Its characteristics were not changed at all.

THEORETICAL CONSIDERATIONS

It seems worth while now to examine the experimental evidence so far obtained, in search of indications as to the probable nature of the processes that underlie the photovoltaic effect. In discussing photovoltaic effects, it is usual to divide the phenomena into two classes: (a) the group in which the electrode is the light-sensitive part of the cell (this is the type discovered by Becquerel); and (b) the type in which the electrolyte is the sensitive part. But the Grignard cells containing solutions of substances like phenylmagnesium bromide, which transport little or no effect with the electrolyte but instead seem to form a sensitive layer on the surface of an otherwise inert electrode, seem to belong in a third class, or at least in a very special subdivision of the second. The dry cells containing substances like cuprous oxide or selenium, but no electrolyte, seem to belong in a still different class, which quite possibly should include some of the cases usually placed in the first group. While many authorities regard the last group as photoelectric rather than photovoltaic in nature, they are placed in the latter class here because of the very great resemblance of their behavior to that of other kinds of photovoltaic cell. The points of resemblance may be stated, for emphasis: (a) the effect observed is a change in electromotive force; relatively large currents can be obtained, but the currents are not always proportional to the illumination; (b) the responses occur with wavelengths too long to excite a surface photoelectric effect in the substances concerned, so that it must be explained by a special internal photoelectric effect if it is due to such an effect; (c) the maximum electromotive force developed is roughly proportional to the logarithm of the illumination, and not a linear function of it, nor is it a linear function of the frequency; (d) the maximum current obtainable is likewise not always proportional to the illumination, at least for high intensities of illumination, but is more nearly proportional to the logarithm of the illumination; (e) the E.M.F. decreases and sometimes actually reverses on long-continued illumination; (f) the response shows a time lag so great that such cells cannot follow light variations of frequency very far above 1000 per second. It is of course true that dry cells show differences in behavior from that of the other classes: they respond and recover more rapidly; the response and recovery curves are somewhat different in shape, possibly indicating a different mechanism for the response; and they show relatively large decreases in resistance when illuminated.

The statements which follow are intended to apply primarily to the effects observed in Grignard solutions, although they apply to a certain extent in a great many other cases. It is not yet possible to give an entirely satisfactory theory of all photovoltaic effects. The writer regrets sincerely that the severe limitations of available space at present necessary have compelled omission of adequate review or reference to the many theories presented by other workers. A picture is here suggested tentatively as being a probable one; it necessarily contains many elements suggested by other workers, but contains a few points that are apparently new.

There are strong reasons for doubting that the effect can be due simply to the emission of electrons under the influence of light. One such reason is the existence of "Minchin reversals," in which the photovoltaic E. M. F. reverses its direction if the illumination is continued. This may not be a conclusive argument, since it has been shown earlier in this article that the same type of reversal can be obtained from the "dry" type of photovoltaic cell, in which the effect is usually explained as being due to the emission of photoelectrons at a barrier layer. However, it may be that this commonly accepted explanation of the action in dry cells is incorrect. Another reason for doubting the simple electronic explanation, in the present case, is the fact that some of the solutions carry the effect with them, when circulated, so that a previously illuminated solution can affect an electrode in the dark, just as if the electrode itself had been illuminated. Not all of the solutions seem to be able to do this; but the fact that some of them do suggests that the effect depends in some way on the formation of either ions or excited molecules by the light. Other reasons for doubting the electronic theory are suggested in the second paragraph above; the theory is quantitatively unsatisfactory in several respects.

The suggestion that light actually ionizes the solutions seems to be definitely contradicted by the experimental evidence. If a Grignard cell be regarded as a concentration cell, for the purpose of computing the change in the concentration of the ions controlling the electrode potential that would be necessary to explain the observed changes in E. M. F., it is found that the concentrations would need to change in a ratio which often would exceed a millionfold. From the conductivity, the ionization is already considerable, and any such change as demanded by the theory would almost certainly give rise to a measurable change in the conductivity of the solutions. This point has been tested thoroughly. Hammond (2), in a number of measurements of the resistance of such cells, found that the changes produced by light were very small. In one case a 2 per cent change was observed, but all the others were considerably smaller. Harty (4), in a large number of measurements, found that the changes rarely exceeded one-half of 1 per cent. In the majority of observations, the change was an increase rather than a decrease in resistance, as if the light had suppressed rather than increased the ionization. In view of these facts, it seems more probable that light produces some type of excited molecules, rather than ions.

It is very likely that the electrodes in the Grignard solutions are covered by layers of adsorbed molecules, which probably are not in quite the same state as the molecules in the solution. There are two chief reasons for such a statement. First, the direct-current resistance of the cells often exceeds the electrolyte resistance, as determined by alternating-current methods, by as much as a thousandfold. Apparently the D. C. resistance is due largely to polarization. It can be decreased by the addition of suitable depolarizing substances. Further, the capacitance of these cells, which can be determined simultaneously with the A. C. resistance, proves to be very large, so that the most reasonable interpretation of the observations seems to be that the capacitance is that between electrodes and electrolyte. Since values of as high as seven microfarads per square centimeter have been observed, it appears that the relatively non-conducting film that covers the electrodes is often only a few molecules thick, possibly at times only one. The sensitiveness of the voltage of some of these cells to shaking may indicate that in some cases these surface layers are very loosely held. The variability of the dark voltage suggests that the films may be continually changing. The photovoltaic effect is then visualized as being due to the formation of excited molecules by the light, either throughout the liquid or, in some cases, only in the layer of electrostatically strained molecules making up the surface film on the electrode; the surface-layer molecules are then more or less completely replaced by excited molecules which are formed in the layer or which drift in to it, or else the excited molecules form an additional layer on the electrode surface. There is evidence in the capacitance measurements of Hammond and of Harty that both of these possibilities actually occur. These adsorbed layers of molecules introduce adsorption potentials which must modify the potentials of the cells.

The action of depolarizers in reducing the D. C. resistance of the cells seems to be due to the substitution in the surface films on the electrodes of other molecules which offer less hindrance to the processes which occur at the electrode surfaces in conduction. The depolarizing substances are not good conductors by themselves, and it is found that at the same time that they reduce the D. C. resistance of the cells, they increase the electrolyte resistance, as would be expected from diluting the electrolyte with a non-conducting liquid. The depolarizing action occurs in systems in which there seems to be no possibility of chemical reaction, and no other explanation than the one just suggested has been put forward for such cases.

While the subject is by no means settled, it is probable that no photochemical reaction occurs in the Grignard solutions which is able to explain the observed photovoltaic effects. It is the opinion of the writer, based on a considerable amount of evidence collected from the literature as well as from observation, that even in those cases in which photochemical reactions are known to occur, in most cases a photovoltaic effect exists independently of and in addition to the changes in E. M. F. due to the chemical reaction.

In view of the facts, now well established (new evidence on this point will be forthcoming from the writer's laboratory later), that a photovoltaic effect can exist independently of fluorescence of or any selective absorption of light by the electrolyte, it seems certain that any idea of a necessary association of these phenomena must be abandoned.

A suggestion as to the nature of the excited molecules postulated above may add a clarifying detail to the picture presented. Most writers have suggested simply an electronic displacement for the excitation process. However, such excitation is usually associated with selective absorption, and, judging from the duration of the associated fluorescence, the life of excited molecules of this type is entirely too short to explain the long-continued photovoltaic effects. It seems that for the present purpose something further is needed. Either more stable types of electronic displacement than are known from other phenomena must be assumed, or else other types of excitation must be sought. Now, another type of excitation is known, from its occurrence in connection with the Raman effect. In this type, the atoms which make up the molecules are separated somewhat by the light, and are set in vibration, the frequency of the internal vibrations being related to the characteristic infra-red frequencies of the molecules. Whether excitation of this type is sufficiently long-lived to explain photovoltaic effects is not known. The writer believes that either this type, or a similar type in which the vibration is missing and the life is longer, will be found able to supply the necessary mechanism for explaining photovoltaic effects. For a given molecule, there are as many types of excitation of this sort as there are types of interatomic linkages. It seems necessary, and not unreasonable, to suppose that at least two types of excited molecules are formed in the cases in which reversals occur; if the type which forms more slowly, or which diffuses to the electrodes more slowly, is also the more stable type, so that its effect ultimately outweighs that of the less stable variety, a possible basis is found for at least a qualitative explanation of the reversal phenomena.

The picture suggested has been described very sketchily and with many details omitted, since it is still in the formative stage. It has, however, already justified itself from the point of view that it has suggested many new experiments which have yielded valuable information regarding the photovoltaic effect.

The writer is grateful to Professors O. M. Stewart and H. M. Reese, of the Department of Physics, the University of Missouri, for continued encouragement and support of this work; and to the gradually increasing group of graduate students who by working out important details are making possible more rapid progress on the problem. Thanks are due the Research Laboratory, Incandescent Lamp Dept., General Electric Co., Cleveland, Ohio, and to Mr. Samuel Wein, of New York, for certain materials used in this work.

REFERENCES

(1) DUFFORD, R. T.: J. Phys. Chem. **34**: 1544 (1930); **35**: 988 (1931).
(2) HAMMOND, H. E.: Thesis, University of Missouri, 1929; Phys. Rev. **35**: 998 (1930).
(3) GRUBE AND BAUMEISTER: Z. Elektrochem. **30**: 322 (1924).
(4) HARTY, JOHN HENRY: Thesis, University of Missouri, 1932.

STUDIES IN COPRECIPITATION. VI

INTERNAL STRUCTURAL CHANGES ON AGING OF FRESHLY PREPARED PRECIPITATES

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Studies made in recent years show that the lattice of a real crystal is far from ideal. Crystals seem to be built of submicroscopic or amicroscopic blocks, the so-called Smekal (1) blocks, which fit together like bricks in a wall, giving rise to free spaces in the packing (Lockerstellen). In addition, ordinary crystals very often even contain microscopically visible cavities. A real crystal therefore has a very discontinuous structure and possesses a large internal surface. D. Balarew (2) has strongly advocated the theory that contaminating substances are adsorbed at the internal surface of a crystal, and goes so far as to attribute all coprecipitations to this cause.

In previous studies dealing with the corprecipitation of water and of foreign ions with calcium oxalate, it was found that contaminants appeared to diffuse out of the crystalline precipitates if the latter were allowed to age under the mother liquor before filtration. This phenomenon cannot always be attributed to a recrystallization, for the particle size is often too large for this to occur to any extent. Therefore, under these conditions, it may be assumed that the contaminant actually diffuses out through microscopically invisible cracks and capillaries in the crystals. In other words, the fresh crystals are very imperfect immediately after precipitation, but on standing there is a tendency for the cracks and capillaries to become filled with lattice material, this process resulting in the pushing out of foreign substances. If the perfection of the crystals would take place in such a way that the capillaries were entirely filled with lattice ions, it might be expected that all the foreign material would be extruded. From the experimental evidence presented in this paper it would appear that the perfection does not take place in such an idealized manner; in most cases dams are formed in the capillaries, and these prevent further effusion of adsorbed material from the inside to the outside of the crystals. Such crystals may have a large "isolated interior surface," which no longer is in open communication with the outside. Moreover, a large part of the internal surface becomes isolated during the growth of the crystalline precipitate.

In the first part of this paper experiments will be described in which potassium iodate was added to a freshly formed suspension of calcium oxalate after the precipitation had taken place. After various times of shaking, the iodate in the supernatant liquid was removed by addition of iodide and dilute acid (insufficient to dissolve the precipitate but strong enough to allow a quantitative reduction of the iodate) and then thiosulfate; after the last trace of iodine had reacted, strong hydrochloric acid was added to dissolve the calcium oxalate, and the iodine liberated from the iodate in the precipitate quantitatively determined with dilute thiosulfate solution. In addition, experiments were made in which the effusion of iodate coprecipitated with calcium oxalate was investigated after various treatments. The experimental procedure in the determination of the iodate content of the precipitate was similar to that described above.

I. EXPERIMENTS WITH CALCIUM OXALATE

A. Decrease of amount of coprecipitated iodate in calcium oxalate on standing

Twenty-four cubic centimeters of 0.25 *N* calcium chloride mixed with 10 cc. of 0.050 *M* potassium iodate was treated at room temperature with 20 cc. of 0.25 *N* ammonium oxalate. The precipitate was allowed to stand in the liquid for the period of time indicated in table 1; 40 cc. of 0.10*N* hydrochloric acid and potassium iodide was then added to the mixture. The iodine thus liberated was titrated first with 0.1 *N* thiosulfate and then carefully with 0.005 *N* until all the iodine was just removed (starch as indicator). Concentrated hydrochloric acid was next added to dissolve all the precipitate and to liberate the iodate held internally. The amount of thiosulfate required to titrate the iodine liberated by the internal iodate is given in table 1.

The precipitate obtained under the conditions just described recrystallizes and grows to larger size on standing, as microscopic observations show, so that the decrease in contamination is not due primarily to effusion of impurity from the crystals. These results are recorded for the purpose of comparison with the next series of experiments, which were made under conditions such that there could have been but little recrystallization. The precipitates described in table 2 were obtained by Hahn's procedure at room temperature in the presence of 10 cc. of 0.050 *M* potassium iodate. The time of precipitation was 5 minutes. Twenty cubic centimeters of 0.25 *N* ammonium oxalate and 21 cc. of 0.25 *N* calcium chloride were used, the latter being kept 1 cc. in excess during the addition. The volume at the end of the precipitation was 100 cc.

It is evident that more than 50 per cent of the iodate has escaped from

Hahn's precipitate after twenty-four hours standing. It is improbable that this purification can be attributed to recrystallization, for the crystal size of the precipitate is larger than that of one formed by the ordinary method in the cold and which has stood for a week in solution. It should

TABLE 1

Dependence of amount of iodate in calcium oxalate precipitated cold on time of standing after precipitation

TIME OF STANDING	IODATE IN PRECIPITATE (AS CC. OF 0.005 N THIOSULFATE)	TIME OF STANDING	IODATE IN PRECIPITATE (AS CC. OF 0.005 N THIOSULFATE)
hours		*hours*	
0	14.2	4	10.3
0	13.0	19	8.4
1½	11.8	19	8.65
1½	11.9	70	8.7
1½	11.6	73	8.5
1½	11.5	120	7.8
2	10.5	48*	2.7
4	10.95		

* Liquid diluted to 225 cc. after precipitation. The high dilution decreases iodate concentration in solution and promotes recrystallization.

TABLE 2

Decrease of iodate content in precipitates (prepared according to F. L. Hahn) on standing

NO	PROCEDURE	CC. OF 0.0050 N THIOSULFATE REQUIRED
1	Precipitate dissolved immediately after precipitation	42.9
2	Precipitate allowed to stand in solution from which precipitated, after 40 cc. of 0.10 N hydrochloric acid had been added and iodine removed, for 18 hours. Precipitate then dissolved and titrated with thiosulfate after removing free iodine. When titrated required.................. ...	24.6
3	Precipitate washed to remove iodate and allowed to stand in 100 cc. of solution containing 4 cc. of 0.25 N calcium chloride for 25 hours	Supernatant liquid contained iodate equivalent to 19 cc. of thiosulfate and the precipitate 23.8 cc.
4	As in 3; stood 48 hours	Supernatant liquid then required 21.1 cc. of thiosulfate and the precipitate required 18.5 cc.

also be remembered that Hahn's precipitate formed at room temperature contains very little higher hydrate, so that the purification cannot be ascribed to the transformation of the higher hydrates into the monohydrate.

Precipitates formed in hot solution generally show only a slight loss of iodate or other contaminant on standing at room temperature. The data will be omitted here.

B. Diffusion of iodate into and internal adsorption by pre-formed calcium oxalate

The results to be described furnish good evidence for the existence of internal surface in open communication with the exterior of the crystals of calcium oxalate.

For the purpose of comparison, the results obtained with the precipitate formed in cold solution are presented; these results are neither distinctive nor conclusive, but lend greater weight to the conclusions drawn from the behavior of Hahn's precipitate (table 5). The precipitates were obtained by adding 20 cc. of ammonium oxalate to 24 cc. of calcium chloride, both 0.25 *N*, at room temperature. The time of addition was 1 minute. After the specified time of standing, 10 cc. of 0.050 *M* potassium iodate was added and the mixture shaken as indicated in table 3. To determine the amount of iodate which had gone into the interior of the crystals it was only necessary to add dilute hydrochloric acid (40 cc. of 0.1 *N* was used) and remove the liberated iodine with thiosulfate, then to add concentrated hydrochloric acid to dissolve all the precipitate and finally to titrate the iodine liberated by the iodate in the particles.

The reproducibility of these experiments is not particularly good. The anomalous results are explained by the existence of two opposing effects: diffusion into the crystal versus recrystallization and transformation of hydrates.

The next series of precipitates (table 4) was obtained from hot solution. Ten cubic centimeters of 0.25 *N* ammonium oxalate was added rapidly dropwise to a mixture of 50 cc. of water and 12 cc. of 0.25 *N* calcium chloride heated to 100°C. Twelve cubic centimeters more of calcium solution was then added to the main solution and again precipitated with 10 cc. of oxalate. This particular procedure was used to obtain crystals that would not be too small. The average crystal diameter was 0.5 to 1 micron. No recrystallization was apparent after a day, but it is not possible to say conclusively that none had taken place. The liquid containing the precipitate was cooled immediately after precipitation by cold water. Ten cubic centimeters of 0.050 *M* potassium iodate was added 5 minutes after the end of the precipitation. The amount of iodate that had permeated the crystals was determined in exactly the same manner as described above.

The variation in amount of post-occlusion with time is very regular. The effect of the aging of the crystals is well marked.

TABLE 3

Diffusion of iodate into and adsorption by calcium oxalate precipitated at room temperature

NO.	TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC. OF 0 0050 *N* THIOSULFATE)
1	0 minute	¼ minute	0 15
2	0 minute	1 minute	0 3; 0 45
3	0 minute	2 minutes	0 55
4	0 minute	5 minutes	0 7
5	0 minute	10 minutes	1 0; 1 4
6	0 minute	15 minutes	1 05; 1.1
7	0 minute	60 minutes	1 85
8	0 minute	180 minutes	1 7
9	0 minute	20 hours	4 7; 5 4
10	0 minute	48 hours	5 5; 7 1
11	0 minute	68 hours	8 5
12	5 minutes	15 minutes	0 55
13	10 minutes	15 minutes	0 35
14	15 minutes	15 minutes	0 25
15	30 minutes	15 minutes	0 20
16	60 minutes	15 minutes	0 15
17	80 minutes	100 minutes	0 25
18	200 minutes	24 hours	5 3
19	24 hours	29 hours	3 0
20	26 hours	3 days	0 3
21	48 hours	25 hours	0 5
22	2 days	5 days	0 6; 0 2
23	3 days	5 days	0 3

TABLE 4

Diffusion of iodate into calcium oxalate precipitated hot

TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC OF 0 0050 *N* THIOSULFATE)
5 minutes	5 minutes	0 4
5 minutes	10 minutes	0 55
5 minutes	20 minutes	0 6
5 minutes	30 minutes	1 05
5 minutes	60 minutes	1 1
5 minutes	120 minutes	1 1
5 minutes	180 minutes	1 15
5 minutes	20 hours (not shaken)	1 85
1 hour	20 hours (not shaken)	1 0
1 hour	2 hours	0 9
2 hours	20 hours (not shaken)	0 85
20 hours	2 hours	0 4; 0 5
3 days	2 hours	0 3

Finally we have the behavior of Hahn's precipitate. Twenty cubic centimeters of oxalate and 21 cc. of calcium were added simultaneously to 50 cc. of water at room temperature, the calcium being kept 1 cc. in excess; time, 5 minutes. At the end of the precipitation, 3 cc. more of calcium chloride was added and immediately thereafter 10 cc. of 0.050 M potassium iodate; the mixture was then shaken (table 5). The internal iodate was determined as before.

These results are decisive. The particle size of Hahn's precipitate is large enough to preclude the possibility of any appreciable recrystallization on standing at room temperature. The diffusion of iodate into calcium oxalate is rapid at first and then falls off. More than 25 per cent of the total amount of iodate has entered the crystal 2 minutes after precipitation and 50 per cent after 10 minutes. The aging of the crystals has a very marked effect on the amount of iodate taken up. The permeability of the crystal has decreased to 50 per cent of the original after an hour or two. These effects quite definitely indicate that calcium oxalate crystals have a discontinuous structure and that they tend to perfect themselves on standing in solution.

TABLE 5

Diffusion of iodate into Hahn's precipitate formed cold

TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC. OF 0 0050 N THIOSULFATE)
0 minute	2 minutes	1 2
0 minute	5 minutes	1 5
0 minute	10 minutes	2 1
0 minute	30 minutes	2 4
0 minute	60 minutes	3 15
0 minute	2 hours	4 05
0 minute	21 hours	3 7
20 minutes	10 minutes	1 6
40 minutes	10 minutes	1 0
70 minutes	10 minutes	0 9
20 minutes	2 hours	2 7
40 minutes	2 hours	2 0
1 hour	2 hours	1 75
2 hours	2 hours	1 6
4 hours	2 hours	1 0
20 hours	2 hours	0 4
44 hours	2 hours	0.25

DISCUSSION OF THE RESULTS

1. Table 1 shows that calcium oxalate freshly precipitated at room temperature from fairly concentrated solutions loses fairly much occluded

iodate on aging; e.g., immediately after precipitation the amount of iodate corresponds to 14.2 cc. of 0.005 N thiosulfate, but after a few days equilibrium is reached, and the figure falls to 7.8. The case here is rather complicated, since the primary precipitate consists of the higher hydrates of calcium oxalate and these undergo transformation into the monohydrate on standing, accompanied by an entire structural change and recrystallization. Table 3 shows the pronounced porous character of calcium oxalate formed under the above conditions. The amount of iodate diffusing into, and being adsorbed at, the internal surface continually increases with the time of shaking and finally, after about two days, reaches a value almost identical with that found in calcium oxalate containing coprecipitated iodate, shaken for two days (see table 1).

From this behavior it is not justifiable to infer, however, that the processes of the effusion and diffusion are reversible, because other factors, such as transformation of higher hydrates with recrystallization, play a predominating rôle here. The figures in table 3 indicate that the changes take place within a short time after precipitation.

2. Table 2 shows the slow effusion of coprecipitated iodate from calcium oxalate prepared at room temperature according to F. L. Hahn's procedure. Although no recrystallization takes place here on aging, the iodate content has decreased to about half of its original value after two days. The reverse process, namely, the diffusion into, and adsorption of iodate by, the internal surface is demonstrated by the figures in table 5. The aging process takes place very rapidly. Comparison of the amount of iodate adsorbed at the internal surface after a day (table 5, 3.7 cc.) with the amount of coprecipitated iodate in the crystals after the same period (table 2, 24.6 cc.) indicates that on aging only a small part of the capillaries is filled by lattice ions, and that the "isolated internal surface" is fairly large. Actually most of the iodate coprecipitated is buried within the crystal and has no chance to escape.

3. Table 3 shows that calcium oxalate precipitated at 100°C. and allowed to stand at room temperature takes up only a very small amount of iodate. In agreement herewith it was found in the previous paper that calcium oxalate prepared under the above conditions loses hardly any coprecipitated iodate, if allowed to age at room temperature. Still the amount of coprecipitated iodate is fairly large (compare table 1 in previous paper (3)), thus showing that the "isolated internal surface" of calcium oxalate precipitated at 100°C. is fairly large and that the iodate is buried within the crystal. The internal surface in open communication with the outside is distinctly smaller than the same of a precipitate prepared at room temperature according to Hahn, even though the latter has a larger crystal size. (Compare tables 4 and 5.)

4. Summarizing, it appears that: (a) Coprecipitated ions quite gener-

ally are adsorbed at the internal surface. (b) A distinction is to be made between (1) internal surface in open communication with the exterior of the crystal, and (2) isolated internal surface. A freshly prepared precipitate very rapidly undergoes internal structural changes that result in an increase of the isolated internal surface and prevent any further effusion of coprecipitated material from within, or diffusion into, and adsorption of ions at its internal surface. The most effective purification of a precipitate is to be expected if the crystals by a slow dissolution and deposition process undergo an entire recrystallization. Calcium oxalate precipitated at 100°C. and aged at room temperature loses hardly any coprecipitated iodate, whereas an effective purification is achieved if the digestion is carried out at higher temperature for a longer time. Under the latter conditions a real recrystallization takes place.

II. PHENOMENA WITH POTASSIUM PERCHLORATE–PERMANGANATE

To confirm the interpretation of the phenomena described with calcium oxalate and potassium iodate, experiments of a similar nature were made with potassium perchlorate and potassium permanganate. The object of these experiments was to determine whether permanganate could diffuse into crystals of potassium perchlorate and be adsorbed internally. If fractures and discontinuities exist in a real crystal of potassium perchlorate, such a crystal placed in a saturated solution of potassium perchlorate containing dissolved potassium permanganate should become stained by the latter. Those two salts are strictly isomorphous and if the effect expected actually exists it should be plainly shown by this pair.

No detailed description of the experiments and the results will be given here—only the salient facts. It was found that crystals of C.P. potassium perchlorate immersed in a saturated solution of the same salt in 0.1 *N* potassium permanganate for a short time—an hour was sufficient—were colored distinctly pink after removal from this solution and after washing with a saturated solution of potassium perchlorate to remove adhering permanganate. Recrystallized potassium perchlorate obtained by evaporating a solution of the salt at room temperature also took up permanganate, but only slightly, so that the crystals were only faintly tinted. If the recrystallized perchlorate was ground in a mortar to give fragments 10 to 100 microns in diameter and these placed in permanganate as before, then it was found that so much potassium permanganate penetrated the crystals that they were colored a vivid red. The permanganate was actually in the interior of the crystals and not at or near the surface, as was proved by taking the colored crystals and shaking them with a volume of water insufficient to dissolve them all. The fragments remaining, though greatly reduced in size, were still colored. Even more drastic treatment failed to remove the color; the red crystals were shaken with a dilute solution of hydrochloric acid and hydrogen peroxide; after a week in this mixture the perchlorate was still strongly colored. Microscopic examination of the colored crystals in reflected light under low magnifications showed that they were homogeneously colored, although some fragments were more strongly colored than others. It is impossible that the coloration of the crystals can be due to permanganate seeping into microscopically visible cavities or cracks.

Beyond a manner of doubt, the permanganate has diffused into microscopically invisible breaks, faults, fractures, discontinuities, or capillaries in the lattice of the perchlorate and has been adsorbed at the internal surface. The phenomenon is not simply one of diffusion alone, for then any imperfect crystal would be colored by permanganate. This was found definitely not to be true. Thus, ground sodium chloride kept in permanganate for a long time remained perfectly uncolored except for an isolated particle or two which had been colored by permanganate that had penetrated into some microscopic crack or cavity. The coloration of a crystal appears to be dependent upon adsorption or incorporation of the colored substance in the lattice. Thus in the case of potassium perchlorate–permanganate, the permanganate, being isomorphous with the first-named salt, will tend to perfect the lattice of this crystal if given the opportunity to do so, i.e., a real crystal of potassium perchlorate immersed in permanganate will be colored by the latter as a consequence of the building up of the lattice. If this be the correct explanation, an imperfect crystal of potassium perchlorate allowed to stand in its own saturated solution should no longer be able to take up permanganate. This was verified. Ground crystals of perchlorate which became strongly colored if first placed in potassium permanganate would no longer take up this substance to more than a very slight extent if first immersed in a saturated solution of potassium perchlorate. The behavior is very striking. The explanation is obvious. When the imperfect crystals were kept in contact with saturated perchlorate, potassium and perchlorate diffused into the discontinuities and filled them by building up the lattice. Permanganate was therefore unable to color the crystals when they were later brought into contact with it. It is evident that crystals of perchlorate which have formed by slow evaporation and which have stood for some time in the saturated solution should take up but little permanganate as already described. Crushing the crystals of the salt should expose the openings of more internal surfaces. Therefore the ground crystals should be colored much more strongly, as was actually found. It is also possible that the stress of grinding causes more faults to appear in the lattice.

The first well authenticated instance of artificial coloration of a crystal appears to have been reported by Vater (4), who found that an artificial crystal of calcite immersed in Thoulet's liquid (a solution of mercuric iodide in potassium iodide) became colored yellowish-brown; the coloration was hastened by boiling the crystals with the solution. Cleavage fragments of Iceland spar became similarly colored. The coloring was entirely homogeneous; the crystals were pleochroic. The last observation is especially worth noting. If the crystals were immersed in water they became colorless after a time. The coloration of Vater's crystals was probably due to iodine.

Retgers (5) emphasized the extreme importance of these results. Strangely enough these observations of the permeability of crystals to solutions do not appear to have aroused much attention. The number of instances of artificial coloration of crystals has remained small.[1] Instances of permeability of crystals to gases are also known, for example, oxidation and change of color of olivine kept in the atmosphere. These facts all speak for a mosaic structure of real crystals.

III. PHENOMENA WITH BARIUM SULFATE–POTASSIUM PERMANGANATE

D. Balarew (2) found that freshly precipitated barium sulfate allowed to stand in potassium permanganate solution was able to take the latter substance into the crystals and give a colored precipitate; he also noted the effect of aging and drying. Such treatment diminished markedly the power of barium sulfate to become colored. Experiments of a similar nature have been made in this laboratory; they can be carried out in a very simple way and offer a striking demonstration of the secondary structural changes taking place in a fresh precipitate on aging. Freshly prepared barium sulfate shaken immediately after precipitation with a permanganate solution assumes a slightly pink color after a few minutes. The intensity of the latter—an indication of the amount of permanganate in the crystals—increases with time, and approaches a maximum after a day or two. Such a precipitate after washing is still red, and retains the color if shaken for a week or longer with a solution of hydrogen peroxide in strong hydrochloric acid. If the barium sulfate is allowed to stand after precipitation for some days and then treated with permanganate, hardly any of the latter compound is taken up, thus showing that the porous character has materially decreased or that most of the pores have been blocked by dams of barium sulfate.

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[1] Toward the end of the nineteenth century the European jewelers were alarmed by reports that yellowish diamonds were being transformed into clear colorless ones by immersion in solutions of blue dyestuffs Retgers (5), who mentions this incident, regarded it as quite possible that the dye had actually diffused into the crystal in these cases and rendered the diamond colorless (blue and yellow being complementary colors). It appears improbable that a film of dye on the exterior could produce this effect. The alchemists were familiar with the decoloration of yellow diamonds by indigo solution (Ferrandus Imperatus, 1695). (See Janettaz: Bull soc min. 14, 65 (1893).)

It may be mentioned in conclusion that ground crystals of potassium sulfate kept in potassium chromate and potassium manganate solutions become faintly yellow and bluish-green respectively. A more thorough study of internal adsorption by crystals and of a secondary structural change taking place in a fresh precipitate is planned for the future.

SUMMARY

1. A fresh precipitate of calcium oxalate or barium sulfate prepared at room temperature forms very inhomogeneous crystals, showing a porous structure. Diffusion of solution into the capillaries followed by adsorption of solution at the internal surface takes place, if the adsorbent is added after the precipitation. Precipitates prepared at 100°C. show a similar behavior, but one not as pronounced as when obtained at room temperature from relatively concentrated solutions.

2. Freshly prepared precipitates on aging undergo rapid structural changes which result in an incomplete perfection of the crystals. Only a small part of the capillaries is entirely filled by the lattice material, most of them being blocked by the latter, thus isolating the internal surface from the outside. The *isolated internal surface* is much larger in a precipitate obtained from hot than from cold solutions.

3. Coprecipitated foreign substances in crystalline precipitates are adsorbed on the internal surface. A purification occurs on aging by effusion of part of the contaminants through the capillaries; the impurities at the *isolated internal surface,* however, cannot be expelled.

4. A slow recrystallization of a precipitate via the solution yields relatively perfect and pure crystals.

5. Most crystalline salts may be expected to have a relatively large isolated internal surface. The latter can be partly exposed by grinding the crystals to smaller dimensions.

REFERENCES

(1) SMEKAL, A : Physik Z. **26,** 707 (1925); Z angew. Chem. **42,** 489 (1929); Z. Elektrochem. **35,** 567 (1928).

(2) BALAREW, D.: Kolloidchem. Beihefte **30,** 249 (1930); **32,** 304 (1931); **33,** 310 (1931).

(3) KOLTHOFF, I. M , AND SANDELL, E. B.: J. Phys. Chem. **37,** 443 (1933).

(4) VATER: Z. Krist. **24,** 366 (1895).

(5) RETGERS: Z physik. Chem. **20,** 534 (1896).

THE INFLUENCE OF COMBINED OXYGEN ON THE DETERMINATION OF VAPOR ISOTHERMALS ON POROUS SOLIDS. II

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INTRODUCTION

As a result of the investigation carried out on charcoal (1), it was decided to employ silica gel to see if the step-like structure of the isothermal could also be obtained in this case by the modified static technique. The apparatus and general methods used were identical with those in the previous paper, except that the evacuation was carried out at 110°C. A further slight alteration in technique was also necessary, since carbon tetrachloride and water vapors (displaced from the gel) cannot be satisfactorily separated by a refrigerant. It was found also that when carbon tetrachloride was heated to 100°C. in the closed container it reacted with the water in the gel, giving rise to phosgene and hydrochloric acid. The container was charged and heated to 100°C. with the tap closed as before and then opened with liquid air on the freezer and as much vapor drawn off as possible. This was pumped away and the gel charged with a fresh sample of carbon tetrachloride. In this way displaced water, hydrochloric acid, and phosgene were removed. It was realized that this form of flushing out might be too drastic in the present case, thereby causing the gel to deteriorate. The water in the unevacuated gel will be held in two ways, partly as adsorbed vapor and partly as a constituent of the gel structure. Admittedly the two forms merge, since the adsorbed molecules which are directly attached to the active centers must be so strongly held that they may be considered to be quasi-chemically attached and therefore similar to the structural water. If the carbon tetrachloride reacts with the structural water it will cause the gel to deteriorate, but if it only reacts with the adsorbed water, it will cause a cleaning-up of the surface, thereby increasing the capacity of the gel.

In any case the adsorbed water will be driven off and that is the first object of this investigation—the attainment of a surface free from foreign adsorbed matter.

EXPERIMENTAL

Carbon tetrachloride isothermals on silica gel at 25°C.

A sample of just over 6 g. of gel was evacuated at 110°C. to a pressure of 9×10^{-4} mm. It was then charged with carbon tetrachloride at 100 mm. pressure, the container tap closed, and the vessel heated at 60°C. for three hours. The container was then opened with liquid air on the freezer and as much vapor as possible removed. This was pumped away and the container recharged at 50 mm. The same procedure was adopted as before and it was again charged at approximately 4 mm. at 25°C., the initial quantity of carbon tetrachloride adsorbed being 150.6 mg. per gram. The isothermal consisted of a desorption curve, followed by resorption to a much higher pressure than previously and further desorption, and is shown in figure 1.

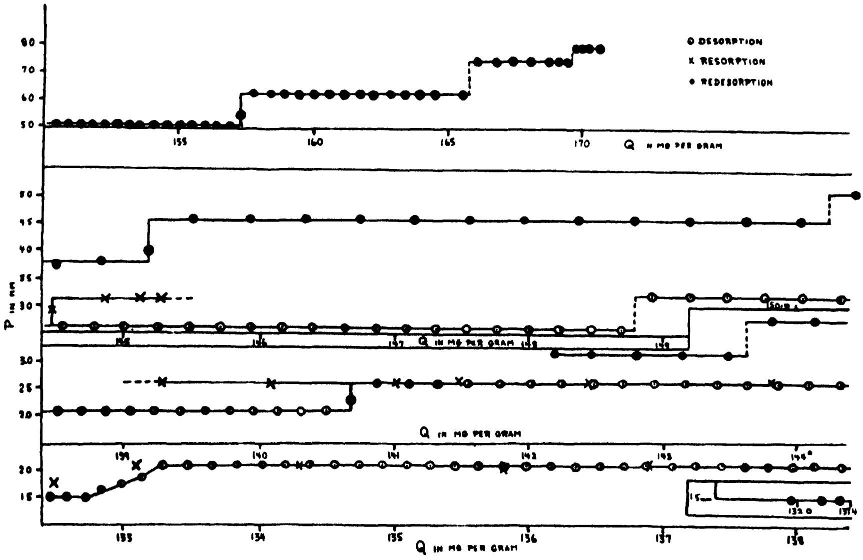

Fig. 1

The complete isothermal comprises 175 points taken over a pressure range of 7 mm. The agreement between the calculated quantity values and those obtained by weighing is good.

Calculated quantity	*Quantity by weight*
145 27 mg. per gram	145 3 mg. per gram
142 18 mg. per gram	141 8 mg. per gram

Equilibrium was almost as rapid as in the experiment on charcoal (1) in the case of desorption, but sorption was definitely slower, taking a quarter of an hour to reach equilibrium, after which no change was observed after standing for twenty hours.

The isothermal was not found to be reproducible, although the pressures at which the breaks occur remained the same, whether on sorption or desorption curves. With successive sorptions or desorptions, the quantity for any given pressure decreases, the gel thus becoming definitely poorer for carbon tetrachloride. From this it would appear that the latter is continuously removing water from the gel, including some of the structural water. This will be dealt with later in the discussion of the benzene isothermals. A few points were determined at lower quantity values to ascertain the pressures at which the breaks occur. The values for the latter in the different series are given in table 1, together with those obtained by the modified retentivity technique.

TABLE 1

Pressures (in millimeters) at which the breaks occur

STATIC			MODIFIED RETENTIVITY
Desorption	Resorption	Redesorption	
		7.96	
		7.44	
		6.28	
		5.10	
		4.60	4.61
		3.78	3.77
3.19	3.13	3.14	3.15
2.59	2.62	2.56	2.64
2.08	2.07	2.08	2.06
1.50		1.51	1.45
		1.18	1.14

The agreement in all cases is good, especially in view of the fact that for the final desorption curve of the static experiment, the gel was charged to 50 mm., whereas in the retentivity experiment it was charged at 8.4 mm. The quantity of vapor adsorbed at 50 mm. was 170.7 mg. per gram. The sequence of breaks has been plotted against the pressures at which they occur (figure 2). As will be seen, a smooth curve results within experimental error. In figure 3 comparison is made with an isothermal determined by the modified retentivity technique and one obtained by the static technique without employing any flushing of the gel, the individual points being plotted in the latter case only.

The latter was carried out some years ago and it was concluded that the isothermal gave a smooth reversible curve. It was seen, however, by comparison with the later retentivity work, that the whole range covered corresponded to a vertical portion of the isothermal. In each case the initial charging pressure was the same. In view of this result it was deemed advisable to repeat the benzene isothermal by the new static technique.

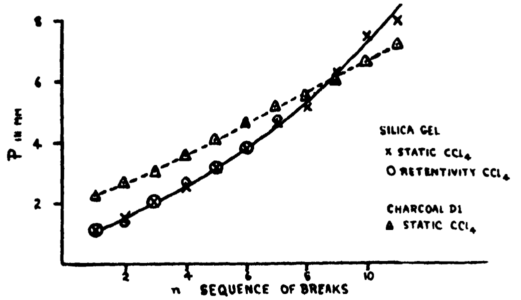

FIG 2

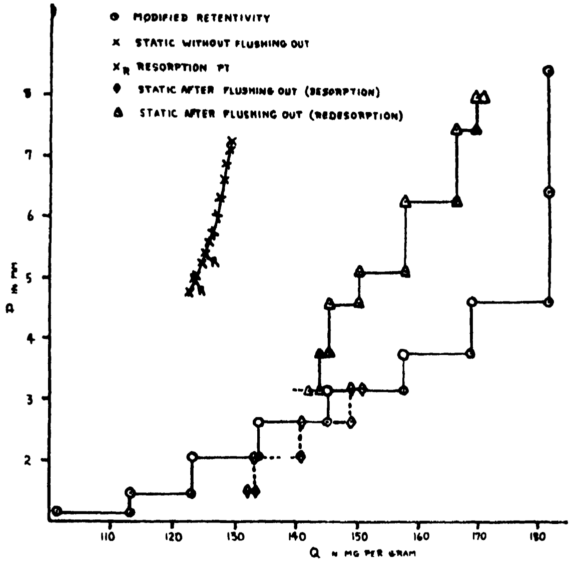

FIG 3

Benzene isothermals on silica gel at 25°C.

Seven and four-tenths grams of gel was evacuated to 1 × 10^{-3} mm.[1] at 110°C. and charged to 42 mm. pressure at room temperature. The tap was closed and the gel heated to 50°C. for two hours. It was then opened with liquid air on the freezer and as much benzene and water removed as was possible. This was pumped away and the gel recharged to 50 mm. pressure, and the container heated at 230°C. for three hours with the tap shut as before. It was then opened with liquid air on the freezer and as much vapor removed as was possible. The gel was now charged at 10.1 mm. and a desorption isothermal carried out. (Figures 4 A and 5 A.)

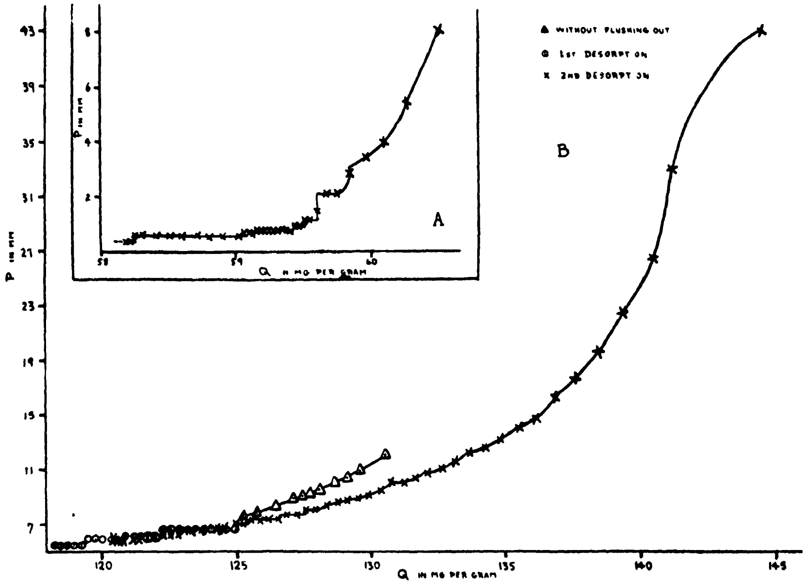

Fig. 4

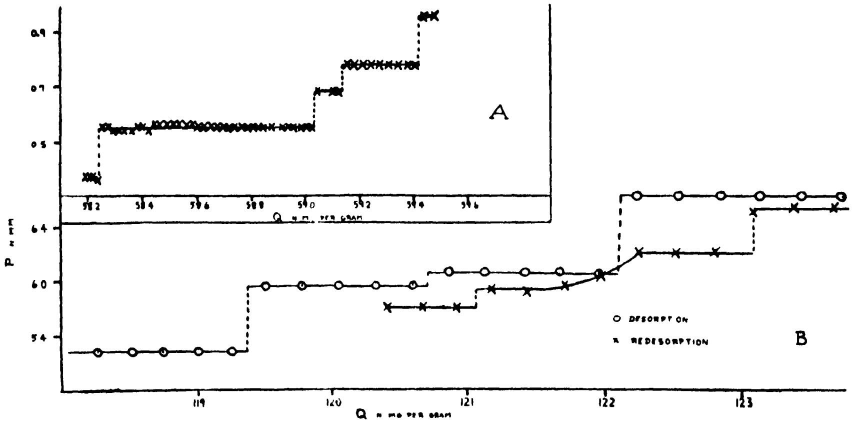

Fig. 5

The initial quantity sorbed was 60.9 mg. per gram and the final 58.2 mg. per gram (58.19 by pressure change method). Reference to figure 5 A shows the isothermal to be quite definitely rectangular in shape.

A second sample of gel (6.56 g.) was evacuated to 8×10^{-4} mm. at 110°C. and charged at room temperature to 20 mm. The tap was then shut and the temperature raised to 100°C. for two hours. All vapor was removed as in the previous case and the gel recharged to 50 mm., the initial quantity being 125.6 mg. per gram. A desorption isothermal was carried out, the final quantity being 117.5 mg. per gram (118.01 by the pressure change method). The gel was then recharged to 50 mm., the quantity adsorbed being 145.4 mg. per gram, and a desorption isothermal carried out to 119.3 mg. per gram (120.39 by pressure change method). Reference to figure 5 B shows that the steps in the first desorption isothermal are very well defined, whereas they are not quite so definite in the second desorption, although they are undoubtedly present. Insufficient points were taken at higher pressures to identify the breaks, but the curve is definitely discontinuous. In figure 4 B, the previous results (2), which employed no flushing out technique, have been added and it shows that the differences between the isothermals are small at low pressures. The fact that the breaks are not so well defined on the final desorption isothermal is of interest, since equilibrium was not established so rapidly on this curve as in other cases. Previously this fact has been definitely connected with an unclean surface, and thus it would seem that more water has been turned out of the gel by the high pressure charge. This is borne out by the fact that the gel has slightly improved as regards its capacity for benzene. The isothermal of the gel which was flushed out at 230°C. shows that this treatment has been too drastic and the gel has deteriorated. It has been shown (Part I of this series and the present paper) that flushing out at 100°C. gives similar results, whether the charcoal has been previously evacuated to 110° or 800°C. Thus, the effect of flushing out the gel at 230°C. would probably correspond to an evacuation temperature of over 1000°C., and the gel would most certainly break down under these conditions.

A comparison of the effect of recharging on the carbon tetrachloride and benzene isothermals shows that the former is a much more powerful agent for the removal of water from the gel. On recharging with benzene a definite cleaning-up effect was observed, whereas with carbon tetrachloride successive recharges caused the capacity of the gel to lessen. In all these experiments on silica gel the equilibrium has not been established quite so rapidly as on a clean charcoal surface. The reason is obvious, since one can never remove all the water from the gel, hence one can only obtain rectangular breaks on successive sorption and desorption isothermals when it is actually the structural water which is being removed, causing the capacity of the gel to lessen for the given vapor.

Thus isothermals on silica gel cannot be obtained as accurately as those on charcoal, since the surface is never entirely free from foreign adsorbed vapor unless water is the vapor whose isothermal is under determination.

Carbon tetrachloride isothermal on charcoal at 25°C.

A further experiment was carried out with carbon tetrachloride on Charcoal D1 (2) to see whether the C_xO_y, which (Part I) had been removed by 800°C. evacuation followed by flushing with vapor, could be removed by 110°C. evacuation and flushing in a manner similar to the previous experiments with silica gel. Approximately 4 g. of charcoal were evacuated in the usual manner till a pressure of 8×10^{-4} mm. at 110°C. was reached. The evacuated charcoal was then charged with carbon tetrachloride to a pressure of 54 mm. and heated to 50°C. with the container tap closed. This was allowed to cool overnight. After eighteen hours the container was heated to 110°C. for two hours and opened to liquid air for one hour, 30.53 mm. of carbon dioxide being evolved. This carbon dioxide, which was measured by placing melting methylcyclohexane on the freezer, was pumped away and the carbon tetrachloride allowed to stream back on the cool charcoal.

TABLE 2

Carbon tetrachloride isothermal on charcoal

P	Q	P	Q
mm	*mg per gram*	*mm*	*mg per gram*
7 14	307 14	4 10	296 39
7 15	306 18	3 54	295 92
6 60	305 29	3 54	295 45
6 60	304 40	3 54	294 98
6 00	303 59	3 08	294 57
6 00	302 78	3 06	294 16
5 48	302 04	3 02	293 76
5 48	301 30	72 hours rest	
5 18	300 60	3 02	293 36
5 18	299 90	2 62	293 01
4 58	299 28	24 hours rest	
4 58	298 66	2 62	292 66
4 58	298 04	2 62	292 31
4 10	297 49	2 62	291 96
4 10	296 94	2 28	291 66
		2 28	291 36

The container tap was shut and the pressure raised to 100°C. for two hours. The same procedure was adopted as in the previous case, 11.04 mm. of carbon dioxide being evolved. This was pumped away and the carbon tetrachloride allowed to stream back. The container was now heated to 120°C. for two hours, 1×10^{-2} mm. of carbon dioxide being evolved. A total of 41.6 mm. of carbon dioxide has thus been displaced by the carbon tetrachloride after evacuation to 8×10^{-4} mm. at 110°C., as compared with a total of 14 mm. of combined oxygen after evacuation to 2 × 10^{-3} mm. at 800°C. The initial quantity of carbon tetrachloride adsorbed was 308.1 mg. per gram. The isothermal consisted of a single desorption curve and the results are given in table 2.

The quantity value by weight = 291.7 mg. per gram, which agrees with that found by the pressure change method.

It is obvious from the figures that the isothermal consists of a series of steps in just the same way as the isothermal on the 800°C. evacuated charcoal.

Equilibrium was almost instantaneous, similar to when carrying out the carbon tetrachloride isothermal on silica gel. In the 800°C. evacuated isothermal the quantity adsorbed at 5.24 mm. was 266.9 mg. per gram, whereas in the present case the quantity is 301.0 mg. per gram. This is the type of agreement one obtains at lower pressures with two samples of an underactivated charcoal, this difference tending to lessen at higher pressures. Two samples of charcoal A (3) charged at 33 mm. with carbon tetrachloride at 15°C. gave the following figures after drift had been overcome: sample 1, 337.3 mg. per gram; sample 2, 312.5 mg. per gram.

TABLE 3

Pressures (in millimeters) at which the steps occur

110°C. EVACUATION	800°C EVACUATION	
	1st desorption	2nd desorption
7.14		
6 60		
6.00		
5.48		
5 18	5 24	
4 58	4 70	4 71
4 10	4 12	4 12
3 54	3 57	3 56
3 02	3 02	3 07
2 62		2 60
2 28		2 34

A comparison of the pressures at which the steps occur has been made in table 3.

DISCUSSION

Fair agreement has been obtained between the 110°C. and 800°C. evacuation isothermals, showing that either method is effective for removing the C_xO_y. The sequence of the breaks against the pressures for the 110°C. isothermal has been plotted in figure 2.

In view of the many ways in which carbon dioxide has been found to affect the determination of isothermals on charcoal, and water to affect those on silica gel, it appeared advantageous to collect some of these data and present them in the present paper.

In all previous work, the isothermals represent poisoned and not true isothermals. This is most serious in those cases where authors have not adopted any flushing method and particularly so when the original evacuation has been carried out at low temperatures. It is not so serious if the original temperature of evacuation was high, but, even so, the poisoning effect is still present. One can, however, get apparent reproducibility in many cases, but the fact that the isothermal is nevertheless poisoned is demonstrated by the increase of quantity adsorbed in a carbon tetrachloride isothermal after 800°C. evacuation, when compared with one evacuated at 110°C., when using a highly activated charcoal.

A further instance of this (2) was noticed with a water isothermal on Charcoal B (3). Here the isothermal was apparently reversible until the original charging pressure was exceeded, when carbon dioxide was evolved and the isothermal showed that drift had taken place. An isothermal showing further instances of this will be given in Part III of this series.

In this connection a very serious criticism may be made regarding almost all previous static experiments, in that no attempt has been made to separate the vapor concerned from the carbon dioxide and carbon monoxide evolved from the surface of the charcoal, or water from the silica gel. However well the surface may have been evacuated, considerable quantities of gas are evolved from the surface by the action of the vapor whose isothermal is under determination. The author has found 2 mm. of carbon dioxide to be present in the vapor phase after saturating charcoal at a pressure of 16 mm. of water vapor. Considerable quantities have been noted in other cases also (2). It is of interest to mention the extraordinary cleaning-up effect noted in the same paper with amyl alcohol, where a slightly higher charge raised the quantity adsorbed from 133 mg. per gram to 396 mg. per gram. Similar instances have been noted in a recent paper[1] on the sorption of vapors by unactivated charcoal. Again carbon dioxide or the C_xO_y, has been found to exert a very serious influence on both the number and pressures of the breaks. In many instances the pressure of a given break is raised, while in other cases extra breaks are added owing to the presence of carbon dioxide on the charcoal surface. In all cases the resultant isothermals consist of a series of curves until the surface is clean, when rectangular steps will result (Part I of this series). An indication that the surface of the adsorbing body is clean is given by the adsorption being instantaneous whether during sorption or desorption. The same applies if one is freezing out a constituent vapor from a mixture, equilibrium being slow, but if the gas is a pure substance, then equilibrium is instantaneous.

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[1] Submitted to the Transactions of the Faraday Society for publication.

SUMMARY

The effect of flushing out with vapor has been noted in isothermals on silica gel.

The change in the position of the isothermals on recharging with vapor has been examined.

The pressures at which breaks occur in isothermals on silica gel determined by the modified retentivity and static techniques have been compared.

The resultant isothermal, after flushing out a charcoal which had been evacuated at 110°C., has been compared with one evacuated at 800°C. and the pressures at which the breaks occur have been tabulated.

Some effects of carbon dioxide on the determination of isothermals have been noted.

REFERENCES

(1) Burrage: J. Phys. Chem. **37**, 505 (1933).
(2) Allmand and Burrage: Proc. Roy. Soc. London **130**, 610 (1931).
(3) Hand and Shiels: J. Phys. Chem. **32**, 441 (1928).

FORMATION OF SUGARS IN MIXTURES OF TARTARIC ACID AND ALDEHYDES IN TROPICAL SUNLIGHT

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It is well-known from the work of Usher and Priestly (1), and Baly and coworkers (2) that carbon dioxide and moisture under the influence of light are converted into formaldehyde. Moore and Webster (3) claimed to have obtained formaldehyde by exposing solutions of colloidal uranic hydroxide through which carbon dioxide was passed. Dhar and Sanyal (4), and Gopalrao and Dhar (5) have made extensive investigations on this point and established the formation of formaldehyde from water and carbon dioxide under the influence of light and photosensitizers, such as chlorophyll, ferric chloride, zinc oxide, methylene blue, methyl orange etc.

The conversion of formaldehyde to sugars under the influence of light has been reported by Baly and coworkers (2), Dhar and Sanyal (4), and Gopalrao and Dhar (5).

That some of the aliphatic acids, such as tartaric, acetic, and oxalic acid and others, decompose in the presence of light and give carbon dioxide is also known from the work of Ciamician and Silber (6), Pierce and Morey (7), and others.

It occurred to the author that in such cases the carbon dioxide molecule, just at the time of its liberation from the acid molecule, might be in a more reactive condition than the ordinary carbon dioxide molecule, and in the presence of strong illumination might easily be converted into sugars, without the aid of any photocatalyst.

The results obtained in an investigation carried out with a view to test the above idea are embodied in the present paper.

EXPERIMENTAL

Aqueous solutions of tartaric acid, aldehydes, alcohols, and mixtures of tartaric acid with aldehydes or alcohols were exposed to sunlight with and without photosensitizers in sealed tubes of soft glass, Pyrex conical flasks covered with beakers, and quartz vessels. Portions of the same solutions were kept in bulbs and conical flasks also in the dark. The solutions exposed and unexposed were examined periodically and simultaneously.

Benedict's[1] solution was used to test sugars, as Fehling's solution is also reduced by formaldehyde. In the experiments carried out in darkness no sugar formation was detected.

TABLE 1

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Tartaric acid alone... .	15	No sugar detected
* Tartaric acid alone.	125	No sugar detected
2. Tartaric acid + zinc oxide ..	15	No sugar detected
3. Tartaric acid + ferrous sulfate.	15	No sugar detected
4. Tartaric acid + sodium bicarbonate.	100	No sugar detected

TABLE 2

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Formaldehyde alone.	15	Formic acid detected; no sugar
* Formaldehyde alone.	125	Formic acid detected; no sugar
2. Formaldehyde + zinc oxide .	15	Formic acid detected; no sugar
* Formaldehyde + zinc oxide .	125	Formic acid detected; no sugar
3. Formaldehyde + calcium carbonate	15	No sugar detected
4. Formaldehyde + magnesium carbonate.	15	No sugar detected
5 Formaldehyde + zirconium nitrate	30	No sugar detected
6. Formaldehyde + cupric nitrate.	30	No sugar detected
7. Formaldehyde + sodium hydroxide	30	No sugar detected
8. Formaldehyde + dilute sulfuric acid	30	No sugar detected
9. Formaldehyde + magnesium nitrate	30	No sugar detected
10. Formaldehyde + tartaric acid.	84	Presence of sugar detected *
* Formaldehyde + tartaric acid.	100	Presence of sugar detected

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[1] In this paper, wherever it has been observed that Benedict's solution is reduced, it has been inferred that reducing sugars are formed. One of the possible objections against this inference may be that in such cases we might actually be dealing with reducing agents which are not sugars. Dhar and Sanyal (J. Phys. Chem. **29**, 926 (1925)), Gopalrao and Dhar (Ibid. **35**, 1426 (1931)) observed that whatever may be the behavior of Fehling's solution, Benedict's solution is not reduced by aldehydes. Baly, Heilbron, and Barker (J. Chem. Soc **119**, 1028 (1921)) reported having obtained tests with Benedict's solution which indicate the formation of sugar being equivalent in reducing power to 0 04 g. of glucose. A large number of experiments carried out by the author also lead to the same conclusion. It appears therefore to be quite safe to conclude that the reducing substances formed in experiments reported in this paper are reducing sugars.

The glass bulbs, conical flasks, and quartz vessels were carefully cleaned with hot chromic acid mixture and washed several times with distilled and finally with conductivity water. The solution of tartaric acid was prepared in conductivity water after boiling vigorously and it was kept in a stoppered Jena glass bottle. The other solutions were also made in conductivity water.

TABLE 3

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Acetaldehyde alone	84	No sugar detected
* Acetaldehyde alone	125	No sugar detected
2. Acetaldehyde + zinc oxide	10	No sugar detected
* Acetaldehyde + zinc oxide	125	No sugar detected
3. Acetaldehyde + potassium nitrate	30	No sugar detected
* Acetaldehyde + potassium nitrate	125	No nitrite detected
4. Acetaldehyde + magnesium nitrate	125	No nitrite detected
5 Acetaldehyde + tartaric acid.	84	Presence of sugar detected
* Acetaldehyde + tartaric acid.	100	Presence of sugar detected

TABLE 4

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Butyl alcohol alone ...	28	No sugar detected
2. Butyl alcohol + zinc oxide.	28	No sugar detected
3. Butyl alcohol + tartaric acid.	47	Presence of sugar detected
4. Amyl alcohol alone.	28	No sugar detected
* Amyl alcohol alone...	125	No sugar detected
5. Amyl alcohol + zinc oxide	28	No sugar detected
* Amyl alcohol + zinc oxide	100	No sugar detected
6 Amyl alcohol + potassium nitrate.	100	No sugar detected
7. Amyl alcohol + magnesium nitrate.	100	No sugar detected
8 Amyl alcohol + tartaric acid	47	Presence of sugar detected
* Amyl alcohol + tartaric acid	100	Presence of sugar detected
9 Ethyl alcohol alone	28	No sugar detected
10 Ethyl alcohol + tartaric acid	24	Presence of sugar detected

The tubes and flasks were exposed to the sun for periods varying from fifteen to eighty-four hours over several days (see tables 1 to 4). Some of the experiments marked with asterisks were repeated and the period of exposure was extended up to one hundred and twenty-five hours to ensure accuracy.

Equimolar solutions of tartaric acid, formaldehyde, butyl alcohol, and amyl alcohol were prepared in conductivity water. One hundred cubic centimeters of the solution of tartaric acid was mixed with 100 cc. each of the formaldehyde, butyl alcohol, and amyl alcohol solutions, respectively. The mixtures were exposed to the sun in quartz vessels for a period of forty hours.

The different mixtures were then titrated with Benedict's solution standardized with glucose solution (0.4294 g. per liter) with usual precautions. The results are given in table 5.

TABLE 5

BENEDICT'S SOLUTION		EQUIMOLAR MIXTURES EXPOSED IN QUARTZ VESSELS
1 cc.	≡	7.5 cc. of (amyl alcohol + tartaric acid in mixture)
1 cc.	≡	9.4 cc. of (formaldehyde + tartaric acid in mixture)
1 cc.	≡	14.8 cc. of (butyl alcohol + tartaric acid in mixture)
5 cc.	≡	7.0 cc. of glucose solution (0.4294 g. per liter)

DISCUSSION OF RESULTS

From tables 1, 2, 3, and 4 it is clear that there is no production of reducing sugars when aqueous solutions of tartaric acid, formaldehyde, acetaldehyde, and alcohols are exposed alone and with photosensitizing agents such as zinc oxide, ferrous sulfate, zirconium nitrate, cupric nitrate, etc.

Sugars are found to be formed only in mixtures of tartaric acid with aldehydes or alcohols.

Table 5 contains the results of semiquantitative experiments carried out.

The reactivity of the nascent carbon dioxide has been reported recently by Rajwansi and Dhar (8) in the formation of formaldehyde by exposing an aqueous solution of sodium bicarbonate.

The absence of sugars in aqueous solutions of tartaric acid or formaldehyde, and the presence of reducing sugars detected in the mixtures of tartaric acid and formaldehyde suggests that by virtue of the reducing properties of the aldehydes the nascent carbon dioxide formed during the decomposition of tartaric acid under the influence of light is reduced to carbon monoxide according to the equation:

$$CO_2 + HCHO = 2CO + H_2O$$

That ultra-violet light converts carbon dioxide to carbon monoxide is shown by Herchefinkel (9) and later by Coehn and collaborators (10).

It is reported by Berthelot and Gaudechon (11) that the presence of reducing substances facilitates the reaction $CO_2 \rightleftarrows CO + O$ Gopalrao and Dhar (reference 5, Part I) have also stated that such a decomposition takes place in visible light in presence of methylene blue or chlorophyll. The nascent carbon monoxide thus formed, owing to the reduction of carbon dioxide by aldehydes, reacts with water giving formaldehyde, and this nascent formaldehyde is polymerized to sugars This explanation can be supported by the schemes of photosynthesis of sugars formulated by Heilbron (12) and Gopalrao and Dhar (reference 5, Part II) They emphasize the reactivity of the nascent state of formaldehyde for the formation of sugars

During the experiments the alcohols are slightly oxidized to aldehydes, and the aldehydes thus formed explain the formation of sugars in the mixtures of tartaric acid and alcohols

SUMMARY

(1) Aqueous solutions of tartaric acid and mixtures of tartaric acid with aldehydes or alcohols were exposed to tropical sunlight for varying periods of time

(2) In solutions containing tartaric acid or formaldehyde only, no trace of sugar could be detected even after very long exposure

(3) Sugar formation has been detected in mixtures of tartaric acid and aldehydes or alcohols

(4) The probable rôle of the aldehydes has been suggested

REFERENCES

(1) Usher and Priestly Proc Roy Soc London **B84**, 101 (1911)
(2) Baly and coworkers J Chem Soc **119**, 1025 (1921)
(3) Moore and Webster Proc Roy Soc London **B87**, 163 (1913), **B91**, 196 (1920)
(4) Dhar and Sanyal J Phys Chem **29**, 926 (1925)
(5) Gopalrao and Dhar J Phys Chem **35**, 1418 (1931)
(6) Ciamician and Silber J Am Chem Soc **44**, 104 (1932) Wm McPherson's lecture on Ciamician
(7) Pierce and Morey J Am Chem Soc **54**, 467 (1932)
(8) Rajwansi and Dhar J Phys Chem **36**, 575 (1932)
(9) Herchefinkel Compt rend **149**, 395 (1909)
(10) Coehn and collaborators Z physik Chem **91**, 347 (1916)
(11) Berthelot and Gaudechon Compt rend **150**, 1690 (1910)
(12) Heilbron Nature, April 14, 1923

THE VELOCITY OF BROMINATION OF ACETOACETIC ETHYL ESTER. I

The Water Reaction

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The object of this work was to make a contribution to the theory of prototropic reactions, and with this end in view it was decided to study the enolization of acetoacetic ethyl ester by measuring the rate of bromination.

In aqueous solution the equilibrium

$$CH_3COCH_2COOC_2H_5 \rightleftarrows CH_3COH\ CHCOOC_2H_5$$

is displaced mainly in favor of the ketone, the concentration of enol being only 0.4 per cent of the total concentration of the ester.

It is well known that bromine reacts practically instantaneously with the enol, while it does not affect the ketone appreciably. This fact is used in Meyer's (1) method for estimating the enol content of the equilibrium mixture by titration with bromine water. If bromine is added to an aqueous solution of acetoacetic ester, the enol is removed by the bromine as soon as it is formed. Therefore, in the amount of bromine used we have a measure of the progress of enolization.

A similar mechanism was first suggested by Lapworth (2) for the reaction between acetone and halogen in aqueous solution. Here the rate of halogenation is a measure of the velocity of enolization of acetone. In agreement with this explanation Lapworth found that the velocity was independent of the concentration and the nature of the halogen.

The kinetic experiments on the reaction of acetoacetic ester and bromine described in this paper agree with the following explanation. The reaction takes place in four steps:

$$\begin{array}{llr}
CH_3COCH_2COOC_2H_5 & \rightarrow\ CH_3COH{:}CHCOOC_2H_5 & (1a) \\
CH_3COH{:}CHCOOC_2H_5 + Br_2 & \rightarrow\ CH_3COCHBrCOOC_2H_5 + H^+ + Br^- & (1b) \\
CH_3COCHBrCOOC_2H_5 & \rightarrow\ CH_3COH{:}CBrCOOC_2H_5 & (1c) \\
CH_3COH{:}CBrCOOC_2H_5 + Br_2 & \rightarrow\ CH_3COCBr_2COOC_2H_5 + H^+ + Br^- & (1d)
\end{array}$$

Thus the reaction does not stop when α-monobromoacetoacetic ester is formed, but this substance takes up more bromine giving the final product α,α-dibromoacetoacetic ester. The rates of bromination of the enol forms of acetoacetic ester (1b) and of monobromoacetoacetic ester (1d) are so great compared with the rates of enolization of the keto forms, that the reactions 1a and 1c determine the velocity of the total reaction. In agreement with this the concentration of bromine was always found to be without influence on the velocity of bromination.

From these assumptions we shall now deduce a mathematical expression for the amount of bromine used by the reaction t minutes after its start. We use the following symbols:

HR = keto form of acetoacetic ester,
HR′ = keto form of α-monobromoacetoacetic ester,
R″ = α,α-dibromoacetoacetic ester,
c = initial concentration of acetoacetic ester (ketone and enol),
ϵ = degree of enolization at keto-enol equilibrium,
t = time in minutes from the start of the reaction,
x = bromine used at the time t in equivalents per liter,
k_0 = unimolecular velocity constant for the enolization of HR (with no added catalyst),
h_0 = the same for HR′, and
$r \equiv h_0/k_0$.
* By an asterisk we denote that the velocity constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343\,k$.

The enol concentration being always 0 after the start of the reaction, we have

$$(\mathrm{HR}) + (\mathrm{HR}') + (\mathrm{R}'') = c \tag{2}$$

From equations 1a to 1d it follows that the bromine used by the reaction is

$$2(\mathrm{HR}') + 4(\mathrm{R}'') = x \tag{3}$$

From equations 2 and 3 we have

$$(\mathrm{HR}) + \tfrac{1}{2}(\mathrm{HR}') = c - \frac{x}{4} \tag{4}$$

The velocity of the consecutive reactions HR → HR′ → R″ is determined by the differential equations

$$-\frac{d(\mathrm{HR})}{dt} = k_0(\mathrm{HR}) \tag{5}$$

and

$$\frac{d(\mathrm{HR}')}{dt} = k_0(\mathrm{HR}) - h_0(\mathrm{HR}') \tag{6}$$

At the time $t = 0$ we have

$$(\mathrm{HR}) = c(1 - \epsilon) \quad \text{and} \quad (\mathrm{HR}') = c\epsilon \tag{7}$$

Integrating equation 5 and using equation 7 we obtain

$$(\mathrm{HR}) = c(1 - \epsilon)\, \epsilon^{-k_0 t} \tag{8}$$

From equations 5 and 6, together with the abbreviation $r = h_0/k_0$, we get

$$\frac{d(\mathrm{HR}')}{d(\mathrm{HR})} = r\,\frac{(\mathrm{HR}')}{(\mathrm{HR})} - 1 \tag{9}$$

Integrating equation 9 and using equation 7 we get (except when $r = 1$)

$$\frac{(\mathrm{HR}')}{(\mathrm{HR})} = \frac{1}{r - 1} + \frac{1 - r\epsilon}{(1 - r)\,(1 - \epsilon)^r}\left(\frac{(\mathrm{HR})}{c}\right)^{r-1} \tag{10}$$

(HR) and (HR′) are now eliminated from equations 4, 8, and 10:

$$\frac{c - \frac{x}{4}}{c} = Ae^{-k_0 t} - \left(A - 1 + \frac{\epsilon}{2}\right)e^{-h_0 t} \tag{11}$$

where we have used the abbreviation

$$A \equiv (1 - \epsilon)\left(1 + \frac{1}{2(r - 1)}\right) \tag{12}$$

Equation 11 may be written in the following way:

$$\frac{c - \frac{x}{4}}{c} = A\,10^{-k_0^* t} - \left(A - 1 + \frac{\epsilon}{2}\right)10^{-h_0^* t} \tag{13}$$

For special values of r the two-membered exponential expression 11 is reduced to a single-membered one. Thus,

$$\text{if } r = \infty, \qquad \frac{c - \frac{x}{4}}{c} = (1 - \epsilon)e^{-k_0 t} \tag{14}$$

$$\text{if } r = 1, \qquad \frac{c - \frac{x}{4}}{c} = \left(1 - \frac{\epsilon}{2} + \frac{1 - \epsilon}{2}\,k_0 t\right)e^{-k_0 t} \tag{15}$$

$$\text{if } r = \tfrac{1}{2}, \qquad \frac{c - \frac{x}{4}}{c} = \left(1 - \frac{\epsilon}{2}\right)e^{-\frac{1}{2}k_0 t} \tag{16}$$

$$\text{if } r = 0, \qquad \frac{c - \frac{x}{2}}{c} = (1 - \epsilon)e^{-k_0 t} \tag{17}$$

In order to show that the kinetic experiments agree with the explanation given above we find such values of the constants ϵ, k_0^* and h_0^* that the experimental values of x and t satisfy equation 13.

At first ϵ is determined. When t is small, equation 13, or the identical equation 11, may be written

$$\frac{c - \frac{x}{4}}{c} = A(1 - k_0t) - \left(A - 1 + \frac{\epsilon}{2}\right)(1 - h_0t) = 1 - \frac{\epsilon}{2} - t\frac{k_0}{2}(1 + (r - 1)\epsilon) \qquad (18)$$

Consequently, ϵ can be computed by plotting $\frac{c - \frac{x}{4}}{c}$ against t for small values of t and rectilinear extrapolation to $t = 0$.

It is more difficult to determine k_0^* and h_0^*. If $h_0^* >> k_0^*$, the second exponential member of equation 13 will decrease rapidly for increasing values of t and will soon be negligible. If we plot $\log \frac{c - \frac{x}{4}}{c}$ against t we should get a curve which approaches asymptotically to a straight line with the slope $-k_0^*$ and makes an intercept $\log A$ on the ordinate axis. From these constants we easily get h_0^* by means of equation 12. In order to test whether all the experimental pairs of values of x and t agree with equation 13 for the values of the constants thus computed we plot

$$\log\left[\frac{c - \frac{x}{4}}{c} + \left(A - 1 + \frac{\epsilon}{2}\right)10^{-h_0^*t}\right]$$

against t. Now, all the points should fall on the straight line previously drawn. If there should be any systematic deviation we may attempt to obtain a better agreement by drawing a new straight line and repeating the operation.

The method here outlined is only applicable when h_0^* is much greater than k_0^*. If they are of the same order of magnitude, the curve will not sufficiently quickly approach a straight line. The following method can be used in all cases. For each pair of values of x and t found by experiment and for a series of values of r we calculate by the method of trial and error the values of k_0^* which satisfy equation 13. Thus, for each pair of x and t a curve through corresponding values of k_0^* and r is determined. We get a family of curves all going through the same point. The coördinates of this point are the values of k_0^* and r which satisfy equation 13 for all the experimental values (figure 1). Actually, we do not find a single point of intersection for all the curves, owing to experimental inaccuracy. However, it is always possible to find the value of r for which the variation of k_0^*

is smallest. In the following treatment of the experimental results we shall see examples of both methods of computation here described. Owing to the mathematical form of expression 13, a small error in x and t will cause rather a great inaccuracy in k_0^* and h_0^* (see figure 1 and table 3).

If equation 13 is satisfied for all the experimental pairs of x and t by $r = \frac{1}{2}$ and a certain value of k_0^*, say $k_0^* = y$, it will, as seen from equations 14 and 16, also be satisfied by $r = \infty$ and $k_0^* = \frac{y}{2}$. If $(y, \frac{1}{2})$ is the common point for all the k_0^*,r-curves, they will all approach the straight line $k_0^* = \frac{y}{2}$ asymptotically when $r \rightarrow \infty$. Consequently, in this case it is impossible to decide from the experiments whether $r = \frac{1}{2}$ and $k_0^* = y$, or $r = \infty$ and $k_0^* = \frac{y}{2}$. It is seen from figure 1, that if the common point of intersection for all the k_0^*,r-curves falls in the interval $\frac{1}{2} < r < \infty$, each curve will cut each of the other curves in another point in this interval, but the new points of intersection are not common for all the curves. It is useful to remember this when computing the constants. Otherwise there is danger of finding a false solution, especially when using the first of the two methods.

EXPERIMENTAL

Materials

Kahlbaum's best preparation of acetoacetic ester was purified in one of the following two ways. (1) With sodium bisulfite as suggested by Elion (3). The ester was dissolved in a little less than the calculated amount of saturated sodium bisulfite solution. An impurity which does not combine with bisulfite was removed by extraction with ether. The ester was again liberated by addition of the calculated amount of potassium carbonate and extraction with ether. After drying with anhydrous sodium sulfate the ether was distilled from the ester. Finally, the ester was distilled several times in vacuo. (2) Through the copper compound. This compound was made by shaking an ethereal solution of acetoacetic ester with an aqueous solution of copper acetate (Wislicenus (4)). The copper compound was three times recrystallized from benzene and then decomposed with hydrochloric acid. The ester was extracted with ether and, after drying with anhydrous sodium sulfate, was twice distilled in vacuo.

Samples of the two preparations were left for fifteen to twenty hours with an excess of sodium hydroxide solution and afterwards titrated with hydrochloric acid. It was found that one equivalent of base hydrolyzed 130.0 g. of the first and 130.1 g. of the second preparation. The calculated molecular weight is 130.08.

The bromine water was prepared from Kahlbaum's bromine "for analysis."

Experimental procedure

A beaker with acetoacetic ester solution (usually 175 cc.), containing in most of the experiments varying amounts of hydrochloric acid or neutral salts, was placed in a thermostat at 24.97°C. or 17.94°C. or in an ice–water mixture. The solution was stirred mechanically. Its temperature could be read off on a thermometer. Bromine water (usually 25 cc. of 0.15 *N*) was brought to the same temperature. The reaction was started by mixing the two solutions. It was stopped after some time (*t* minutes) by adding an excess of allyl alcohol dissolved in water. This reacts instantaneously with the remaining free bromine. The time was measured by means of a stop-watch which had been compared with an accurate pendulum clock. The corrections never exceeded 0.2 second. Immediately after the reaction was stopped, an excess of solid potassium iodide (1 to 2 g.) and a little dilute hydrochloric acid was added. Iodine equivalent to the bromine used by the reaction is liberated

$$CH_3COCHBrCOOC_2H_5 + 2I^- + H^+ \rightarrow CH_3COCH_2COOC_2H_5 + I_2 + Br^-$$

and

$$CH_3COCBr_2COOC_2H_5 + 4I^- + 2H^+ \rightarrow CH_3COCH_2COOC_2H_5 + 2I_2 + 2Br^-$$

The iodine was titrated with 0.05 *N* thiosulfate and starch solution. The liberation of iodine does not take place instantaneously. The thiosulfate was added in small portions, and the titration was considered as finished when the solution stayed colorless for five minutes after addition of one drop of 0.05 *N* thiosulfate. Usually the titration took fifteen to twenty minutes. Dissolved oxygen and small amounts of impurity in the chemicals used may oxidize some iodide during the titration. In order to correct for this error a blank experiment without acetoacetic ester was done for each series of experiments. It used always less than 0.10 cc. of thiosulfate. In the experiments at 0°C. the solution was slowly heated to room temperature during the titration. Both the bromination and the analysis were carried out in diffused daylight or artificial light. Neither the bromopropyl alcohol formed by the reaction between bromine and allyl alcohol, nor the excess of allyl alcohol interfered during the analysis. The former does not liberate iodine from iodide; the latter reacts too slowly with iodine. Fortunately it is unnecessary to know the exact concentration of bromine during the reaction, the velocity being independent of the amount of bromine.

It was found to be important to add the potassium iodide immediately after the bromination was stopped. If the solution was left for some time before analysis, too little thiosulfate was used, and the last part of the liberation of iodine was much slower than usually. In this case it was noticed that the solution had a sharp smell. Probably the bromo- or dibromo-acetoacetic ester is slowly transformed into compounds which react more slowly with iodide. This may also explain why the results of the analysis are lower than expected in experiments where the bromine has reacted for a very long time. With extremely long times of reaction the bromine found by the analysis even decreased when the time of bromination was increased. In such experiments the solution was cloudy after the bromination. This error adds to the difficulty in computing the velocity constants k_0^* and h_0^* from the experimental results.

In a great number of experiments it was shown that the velocity is independent of the bromine concentration. This is seen most distinctly from some experiments carried out in another way. To the solution of acetoacetic ester was added insufficient bromine water, and the moment when the reaction ceased because all the bromine had reacted was determined electrometrically. Into the beaker dipped a platinum electrode, and the solution was connected by means of an agar–agar bridge with a glass containing a solution of iodine and potassium iodide into which dipped another platinum electrode. The electrodes were connected with a galvanometer through a high resistance. As long as bromine was present the galvanometer gave a slowly decreasing deflection. When the last trace of bromine disappeared the zero was quickly passed, and the galvanometer gave a considerable deflection in the opposite direction. The time from the mixing of the solutions until the disappearance of the bromine was measured. Potassium iodide was added to the solution, and the analysis was carried out in the usual way. The time of reaction was varied by adding varying amounts of bromine water in the different experiments. Experiments carried out in this way gave exactly the same results as experiments with an excess of bromine and interruption by means of allyl alcohol. This shows conclusively that the velocity is independent of the concentration of bromine. Consequently, the reaction by which bromine is taken up is very rapid compared with the reaction which determines the actual velocity of the complete process. The allyl alcohol method, being the simplest and most accurate, was used for all the experiments whose numerical results are given below.

The results of a series of experiments on the bromination of acetoacetic ester in water at 17.94°C. are given in table 1. The initial concentration of bromine was 0.025 M, and that of the ester 0.005062 M except in experiments marked thus (†), where it was 0.01736 M. By extrapolation to $t = 0$ it was found that $\epsilon = 0.0034$. By plotting $\log \frac{c - \frac{x}{4}}{c}$ against t, the values $k_0^* = 0.01802$ and $h_0^* = 0.206$ were found. In order to test the agreement with formula 13, $\frac{x}{4}$ was calculated from the formula, using the

TABLE 1

Bromination of acetoacetic ester in water at 17.94°C.

$c = 5.062 \times 10^{-3}$. In the experiments marked †, $c = 17.36 \times 10^{-3}$. $\epsilon = 0.0034$. $k_0^* = 0\ 01802$. $h_0^* = 0\ 206$.

t	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	$A\ 10^{-k_0^* t}$	$\left(A - 1 + \frac{\epsilon}{2}\right) 10^{-h_0^* t}$	$\frac{x}{4} \times 10^3$ (calcd)	$\delta \times 10^6$
†0 083	0 063	0 9964	1 0406	0 0440	0 059	+4
†0 258	0 132	0 9924	1 0328	0 0405	0 134	−2
†0 500	0 240	0 9862	1 0226	0 0363	0 238	+2
†1 00	0 470	0 9729	1 0014	0 0286	0 473	−3
1 00	0 140	0 9725	1 0014	0 0286	0 138	+2
†2 00	0 993	0 9428	0 9607	0 0177	0 990	+3
2 00	0 286	0 9438	0 9607	0 0177	0 288	−2
†3 00	1 540	0 9113	0 9222	0 0110	1 542	−2
3 00	0 454	0 9105	0 9222	0 0110	0 450	+4
4 00	0 618	0 8782	0 8847	0 0069	0 619	−1
5 00	0 786	0 8449	0 8488	0 0043	0 787	−1
6 00	0 943	0 8140	0 8141	0 0027	0 954	−11
7 00	1 118	0 7793	0 7809	0 0017	1 117	+1
8 00	1 277	0 7475	0 7490	0 0011	1 276	+1
10 00	1 575	0 6891	0 6894	0 0004	1 574	+1
12 00	1 851	0 6345	0 6349	0 0002	1 847	+4
15 00	2 226	0 5604	0 5604	0 0000	2 225	+1
18 00	2 552	0 4960	0 4948	0 0000	2 557	−5
24 00	3 090	0 3897	0 3857	0 0000	3 109	(−19)

$\delta_m = 3\ 6 \times 10^{-6}$

TABLE 2

Bromination of acetoacetic ester in 0 050 M potassium bromide at 17 94°C

$c = 5.056$. In experiments marked †, $c = 6\ 275 \times 10^{-3}$ $\epsilon = 0\ 0040$ $k_0^* = 0\ 01780$.
$h_0^* = 0\ 216$

t	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	$\frac{x}{4} \times 10^3$ (calcd)	$\delta \times 10^6$
0 053	0 016	0 9968	0 016	0
0 080	0 019	0 9963	0 019	0
1 00	0 139	0 9725	0 136	+3
2 00	0 291	0 9425	0 288	+3
4 00	0 619	0 8776	0 619	0
6 00	0 948	0 8125	0 952	−4
†8 00	1 570	0 7499	1 575	−5
10 00	1 561	0 6912	1 564	−3
†12 00	2 283	0 6362	2 281	+2
†14 00	2 600	0 5857	2 595	+5
16 00	2 324	0 5404	2 324	0

$\delta_m = 3\ 1 \times 10^{-6}$

values of ϵ, k_0^* and h_0^* here computed. The last column of the table gives the difference δ between the observed and calculated values of $\frac{x}{4}$. The agreement is good, except when $\frac{c - \frac{x}{4}}{} < \frac{1}{2}$. Here the observed values are smaller than calculated from the formula. This discrepancy was mentioned above. In order to express how well the course of the reaction agrees with the formula, we calculate $\delta_m = \frac{\sqrt{\Sigma\delta^2}}{n-1}$, where n is the number of experiments. If we disregard the last experiment, we get $\delta_m = 3.6 \times 10^{6}$.

Table 2 gives the results of a series of experiments in 0.050 *M* potassium bromide at 17.94°C. treated in the same way. It is seen that bromide ions have only a slight effect on the velocity.

TABLE 3

Calculation of k_0^* from formula 13 for different values of r

The same series of experiments as in table 2

t	$k_0^* \times 10^4$						
	$r = 0\ 5$	$r = 2$	$r = 6$	$r = 10$	$r = 12$	$r = 15$	$r = \infty$
1 00	224	216	197	186	181	173	112
2 00	249	230	202	185	179	172	124
4 00	276	243	202	184	179	171	138
6 00	298	245	200	183	179	172	149
8 00	310	245	198	182	178	173	155
10 00	320	243	196	182	179	174	160
12 00	326	241	193	181	179	175	163
14 00	330	238	193	181	179	176	165
16 00	332	235	191	181	179	176	166

The experimental results of this series have also been computed in the second and more difficult way described above. As seen from table 3 the variation of the calculated k_0^* values is smallest when $r = 12$, giving as mean value $k_0^* = 0.0179$ and $h_0^* = 0.21$ in agreement with the values found in table 2. In figure 1 is given a graph of the computation. For simplicity only four experiments are represented. It is seen that each curve cuts each of the other curves in one point in addition to the point of intersection common to them all. As seen from the table and diagram, we may vary r considerably without impairing the constancy of k_0^* appreciably. Therefore, the constants k_0^* and h_0^* are not determined as accurately as might be expected from the good agreement between the observed and calculated values of $\frac{x}{4}$.

Table 4 contains a summary of twenty series of experiments on the bromination in aqueous solutions of hydrochloric acid, sodium chloride, and potassium chloride, all at 18°C., and, finally, of potassium bromide at 0°, 18° and 25°C. The salts were Kahlbaum's or Merck's "for analysis." The initial concentration of acetoacetic ester was usually about 5 × 10^{-3} M, but in a few experiments three to four times as great. All concentrations are given in moles per liter. In our computation of the constants we have disregarded those experiments with long times of reaction where the fall in x mentioned above made its appearance. All the experiments in the first half of the reaction $\left(\frac{c - \frac{x}{4}}{c} > \frac{1}{2}\right)$ have been used. The number, n, of experiments used is given in table 4 for each series. The agreement with formula 13 is always good. The mean value of δ_m for the twenty series of experiments is 3.0 × 10^{-6}. The volume during the reaction being 200

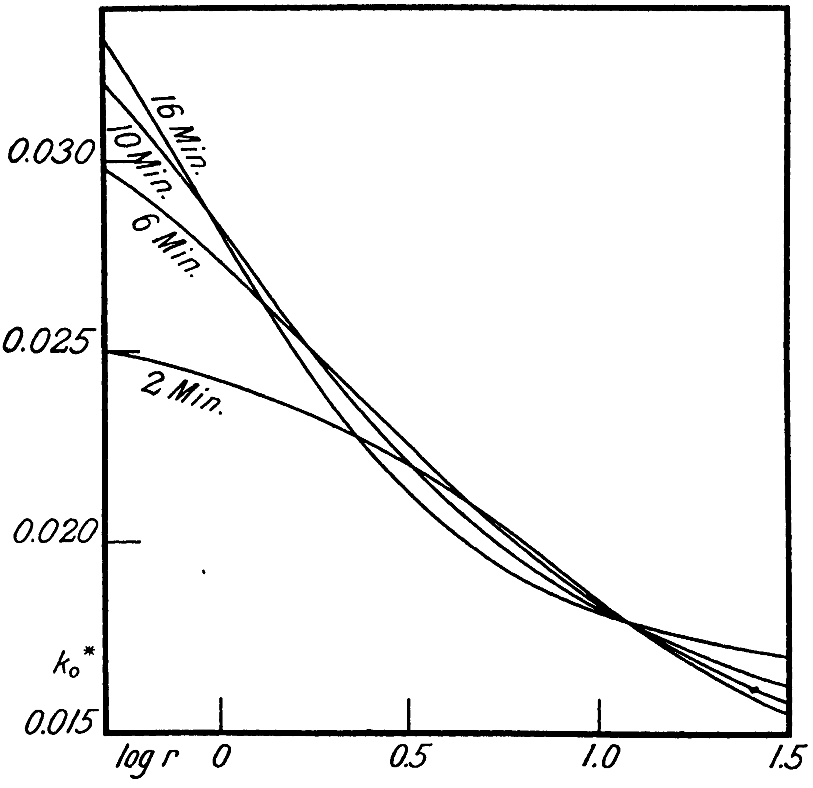

FIG. 1. COMPUTATION OF k_0^* AND r OF THE EXPERIMENTS IN TABLES 2 AND 3

cc., $\delta = 3.0 \times 10^{-6}$ corresponds to 0.05 cc. of 0.05 N thiosulfate. In all the solutions the reaction may be expressed by formula 13 with an accuracy corresponding to the experimental error. The total non-systematical part of the experimental error thus corresponds to an average error of 0.05 cc. on the titration.

In figure 2 the velocity constants k_0^* of the enolization of acetoacetic ester at 18°C. in solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide are plotted against the concentration M of the acid or salt. The decrease in k_0^* caused by the three salts is approximately proportional to the concentration. However, this primary salt effect is not great, only a few per cent in 0.1 M solution. The effect on the enolization of monobromoacetoacetic ester is nearly the same. Thus r is almost constant for all the solutions, as seen from table 4.

TABLE 4

Bromination of acetoacetic ester in water and aqueous solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide

t	SOLVENT	n	ϵ	k_0^*	h_0^*	$\mathfrak{z}_m \times 10^6$	r
degrees C							
17 94	Water	18	0 0034	0 01802	0 206	3 6	11 4
	HCl 0 0424 *M*	16	0 0040	0 01843	0 187	2 6	10 1
	HCl 0 0986 *M*	15	0 0038	0 01869	0 187	4 2	10 0
	HCl 0 1970 *M*	11	0 0038	0 01905	0 191	2 0	10 0
	HCl 0 370 *M*	10	0 0042	0 01955	0 196	2 4	10 0
	NaCl 0 100 *M*	10	0 0037	0 01785	0 215	4 0	12 0
	NaCl 0 300 *M*	10	0 0037	0 01729	0 195	2 1	11 3
	NaCl 0 400 *M*	10	0 0037	0 01704	0 190	2 2	11 2
	NaCl 0 500 *M*	10	0 0037	0 01667	0 186	2 1	11 2
	NaCl 0 600 *M*	10	0 0037	0 01626	0 180	2 4	11 1
	NaCl 0 700 *M*	12	0 0036	0 01592	0 178	2 4	11 2
	NaCl 0 800 *M*	10	0 0036	0 01557	0 174	2 3	11 2
	NaCl 1 000 *M*	9	0 0036	0 01481	0 168	2 6	11.3
	NaCl 2 000 *M*	7	0 0018	0 01133	0 147	3 1	13 0
	KCl 0 596 *M*	10	0 0040	0 01563	0 186	1 2	11 9
	KCl 0 894 *M*	10	0 0036	0 01443	0 174	4 3	12 0
	KCl 1 192 *M*	12	0 0040	0 01337	0 150	3 9	11 2
0 03	KBr 0 050 *M*	12	0 0035	0 00353	0 0425	5 6	12 0
17 94	KBr 0 050 *M*	11	0 0040	0 01780	0 216	3 1	12.1
24 97	KBr 0 050 *M*	13	0 0045	0 03120	0 384	3 5	12.3

Addition of hydrochloric acid causes an increase of k_0^* of the same order of magnitude as the decrease caused by the salts. The effect is so small that it is hardly possible to decide whether it is caused only by a primary salt effect of the hydrochloric acid, or whether a hydrogen ion catalysis has a share in it. If there is any acid catalysis it is very slight. Thus the increase in 0.1 *M* hydrochloric acid is only 4 per cent. For comparison we may mention that the basic catalysis, which we shall deal with in the next part of this paper, is very pronounced. Thus the weak base, the acetate ion, in the concentration 0.1 *M* causes the velocity to rise to about forty times its value in water.

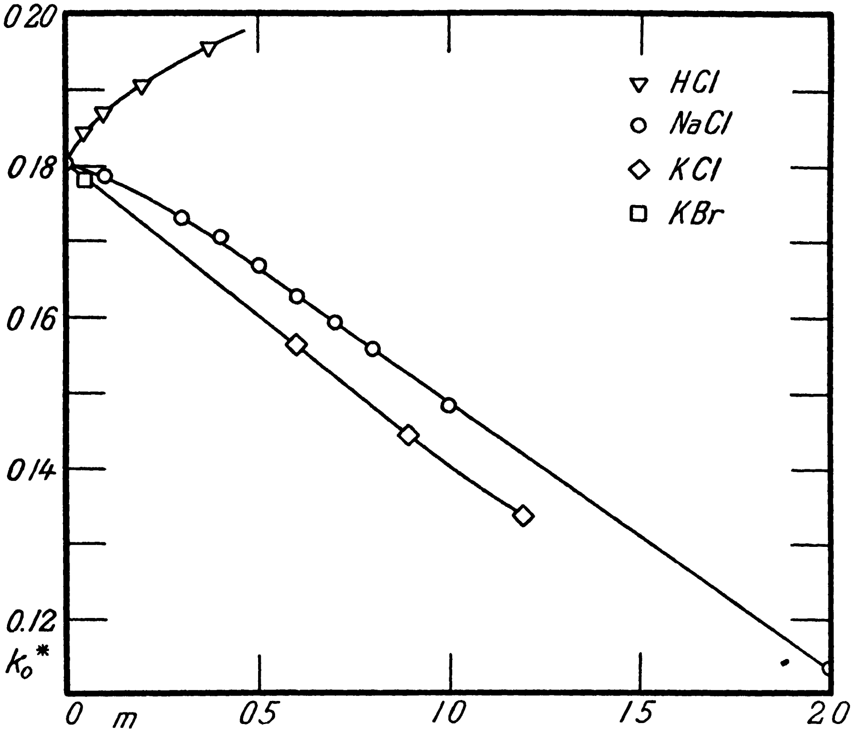

FIG. 2. BROMINATION OF ACETOACETIC ESTER IN SOLUTIONS OF HYDROCHLORIC ACID AND NATURAL SALTS

According to the scheme in equations 1a to 1d small amounts of hydrogen and bromide ions are formed by the reaction. We have seen that the effect of these ions is so small that their formation can have no influence on the velocity.

It is of interest to compare these results with some earlier measurements on the velocity of isomerization of acetoacetic ester carried out by Meyer (5). In one case he dissolves acetoacetic ester, containing 7 per cent of enol, in water at 0°C. and follows the decrease in enol by titration with bromine water at different times (1/6 to 1 minute after dissolving the ester). The reaction being balanced, the unimolecular constant calculated in the usual way is the sum of the constants for the ketonization and for the enolization $k_{\text{ket}} + k_{\text{enol}}$. Meyer finds at 0°C. the constant 2.4, from which he calculates, using $k_{\text{enol}}/k_{\text{ket}} = \epsilon/1 - \epsilon = 0.004$, $k_{\text{ket.}} = 2.4$ and $k_{\text{enol}} = 0.010$, that is, $k_{\text{enol}} = 0.0043$. If, instead of Meyer's value of ϵ, we use the value found in this paper at 0°C., $\epsilon = 0.0035$, we get $k_{\text{enol}} = 0.0036$, in good agreement with the value 0.00357 found here (calculated from our value in 0.05 *M* potassium bromide, assuming that the relative decrease by addition of 0.05 *M* potassium bromide is the same at 0°C. as at 18°C.).

In other experiments Meyer added varying amounts of bromine water to old solutions of acetoacetic ester at 0°C. (in one series at 10°C.) and determined the time when the color of the bromine had just disappeared. However, in his calculation of the velocity constant Meyer takes into account only the enolization of the acetoacetic ester, not being aware that it is followed by the much quicker enolization of the monobromoacetoacetic ester. Here his results are recalculated, taking into regard both enolizations. For comparison values of k_0^* from the experiments in this paper are given in the last column.

	k_0^* (Meyer recalcd.)	k_0^* (Pedersen)
Water 0°C.	0.0031	0.00357
Water 10°C.	0.0088	0.0090
0.1 *N* HCl 0°C.	0.0038	0.00371

While Meyer's experiments in water at 10°C. and in hydrochloric acid at 0°C. agree well with those in this paper, there is a fairly great discrepancy in water at 0°C. From the considerable rise in k_0^* when going from water to 0.1 *N* hydrochloric acid (Meyer actually found by his method of computation an increase of 40 per cent), he concludes that hydrogen ions have catalytic effect. This result is not confirmed by the present investigation.

SUMMARY

In the bromination of acetoacetic ethyl ester four consecutive reactions could be distinguished. (1) The acetoacetic ester is enolized, and (2) brominated to the keto form of α-monobromoacetoacetic ester; (3) this is enolized, and (4) brominated to α, α-dibromoacetoacetic ester. Only (1) and (3) take place with measurable velocity. The unimolecular velocity constants of the enolization of acetoacetic and of monobromoacetoacetic ester in water and aqueous solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide have been computed from the experiments. The reaction is not catalyzed by hydrogen ions to any perceptible degree.

REFERENCES

(1) Meyer, K. H., and Kappelmeyer, P.: Ber. **44**, 2718 (1911).
(2) Lapworth, A.: J. Chem. Soc. **85**, 30 (1904).
(3) Elion, H.: Rec. trav. chim. **3**, 246 (1884).
(4) Wislicenus, W.: Ber. **31**, 3153 (1898).
(5) Meyer, K. H.: Liebig's Ann. **380**, 212 (1911).

THE INFLUENCE OF SMALL AMOUNTS OF DISSOLVED SILICATES ON THE CONDUCTANCE OF CONDUCTIVITY WATER AND VERY DILUTE SOLUTIONS OF ELECTROLYTES

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INTRODUCTION

The magnitude and sign of the solvent correction to be made in conductivity data is sometimes very uncertain, and its application has been the subject of much discussion and controversy in the past few years. This arises mainly from uncertainties as to the impurities present in conductivity water and their reaction with the electrolyte in solution. Kendall's (1) "carbonic acid correction" has not been generally accepted, partly because of the maximum observed at high dilutions in the data for strong acids even after the correction had been made, and partly because some authors have found disturbing factors greater than the carbon dioxide present. Washburn (2) suggests that this "abnormal behavior" is probably due to the presence of some basic or saline impurities, while Whetham and Paine (3) attribute it to a salt, probably ammonium carbonate.

Though it is conceded that carbon dioxide is generally the major impurity, Wynne-Jones (4) has shown a deviation between the calculated and theoretical curves and suggests that solution of silica from the cell walls might cause the variation. Kraus and Parker in their work on iodic acid with concentrations as low as .00005 *N*, using very pure water and cells of quartz, Pyrex, and soda-lime glass have shown that the nature of the cell is of greater importance than the initial conductivity of the water or the carbon dioxide content.

The extent of the solubility or decomposition of glass under the conditions ordinarily met with in conductance work has not as yet been studied very thoroughly. Such measurements would be difficult to make and reproduce, because there are so many factors influencing the decomposition and rate of solution. Glasses also vary much in their physical and chemical constitution, even those of the same brand. Glass in contact with moist air and carbon dioxide is continually being acted upon, giving products which are easily soluble in water. Thus solutions put in such a container, which has not been well leached just before use, will be affected abnormally at first. This phenomenon is easily noticeable by pouring a very dilute solution of hydrochloric acid into a bottle which has been standing open to air. The reduction in conductance at first is comparatively large, changing only gradually thereafter.

Forester's (5) and Walker's (6) work on the solubility of glass under laboratory conditions shows that it is by no means negligible, and that both alkali and silica are taken into solution, probably in the form of a sodium silicate. The nature and behavior of the silicates of sodium in solution has been studied quite thoroughly by Haag (7) and by Harman (8). From their work it has been concluded that the only sodium silicates existing in solution as such are the metasilicate, Na_2SiO_3, and the disilicate, $NaHSiO_3$; that the hydrolysis of Na_2SiO_3 gives rise to $HSiO_3^-$ ions, which do not separate out colloidally; that only ratios larger than $Na_2O:SiO_2 = 1:2$ give appreciable amounts of colloidal silicic acid. In addition, Harman has shown that in dilute solutions of any ratio, practically all the silica exists in the crystalloidal state. Under the term "crystalloidal silica," he classifies definite silicate and bisilicate ions, aggregates of ions carrying an electric charge with or without colloidal silica, i.e., ionic micelles and crystalloidal silicic acid or hydrated silica.

The present investigation is an attempt to show the effect of small amounts of sodium silicates, such as are dissolved from glasses, on very dilute solutions of electrolytes and on conductivity water. Although there is no definite proof that the material dissolved or decomposed from the glass is in the form of silicates of sodium, it is shown from equilibrium relations between the crystalloidal silica and alkali that effectively it is in that form. Further, the solution of glass and change in the nature of impurities in conductivity water with collection and storage in Pyrex and soft glass containers will be demonstrated.

EXPERIMENTAL

The conductivity apparatus was one arranged and set up by Alonzo W. Martin.[1] A telephone head-set tuned to a 1000 cycle E.M.F. from a Vreeland oscillator was used as a detector. To increase its sensitiveness a one-stage audio tube amplifier, as suggested by Hall and Adams (9) was placed in series with the telephone. A Kohlrausch drum-wound slidewire bridge divided in one thousand divisions was calibrated for use by the method of Stronhal and Barus. For the resistance, two calibrated Curtiss coils of capacities 10,000 ohms and 100,000 ohms were used. Adjustable air condensers cut out all capacitance and eddy currents, thereby increasing the sensitiveness and clearness of the minimum point. The whole apparatus was well grounded with a grounding arrangement similar to that suggested by Wagner (10). Measurements were made in a thermostat regulated to 25°C. The dip-type conductance cell with bright platinum electrodes was used so it could be dipped into the solutions through the neck of a well leached liter Pyrex flask. The cell constant was obtained by inter-comparison on a 0.001 *N* solution of potassium chloride, which value checked very closely with that obtained by using 0.0014695 mhos for the specific conductance of the potassium chloride (11). Its value was taken as 0.081402.

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[1] The writer is indebted to Professor Martin for the use of the apparatus.

Stock solutions of hydrochloric acid, potassium chloride, and sodium hydroxide were carefully made up from the C.P. materials. These were measured out in standard calibrated pipettes and diluted to the desired concentration. One liter of the solution was transferred to the conductance arrangement; the whole was well but gently stirred after the addition of each increasing amount of 0.00046 *N* sodium silicate; the electrodes were raised and lowered several times in the solution and a short time was allowed for equilibrium to become closely established, after which all readings were immediately taken. Care had to be used throughout to prevent as far as possible the adsorption of carbon dioxide from the air and to prevent any vigorous motion, since it increases the amount of glass dissolved from the apparatus. Extreme accuracy was not aimed at, since at such high dilutions accurate values of conductance would be of little value, because the exact nature of all the impurities in the water is not known, and the exact behavior of electrolytes at these extreme dilutions is not fully understood. The sodium silicate used was made up from Baker's 40 per cent solution having, according to their analysis, a $Na_2O:SiO_2$ ratio of 1 : 3.22. The normality with respect to sodium was 0.00046.

The conductivity water was obtained from a specially constructed Kraus type still charged with alkali-permanganate. Water ranging in conductance from 0.4×10^{-6} to 1.4×10^{-6} was prepared, and the effect of sodium silicate on conductance of water with different initial conductivities noted. The results are given in graphs (figure 1) rather than in tables, since the nature of the changes is more easily seen and compared. The results showing the effect of small amounts of sodium silicate on the conductance of very dilute solutions of hydrochloric acid, sodium hydroxide, and potassium chloride are given in figures 2, 3, and 4, respectively. In order to demonstrate the rate and extent to which silicates dissolve from Pyrex and soft glass containers, water was left standing in 10-liter bottles, both sealed and open. At various times 1-liter samples were drawn and conductometric titrations run with sodium silicate, as above, to show how much carbon dioxide had been removed by action of dissolved silicates. Many such runs under varying conditions were made, and some representative results are given in figures 5 and 6.

DISCUSSION

From the curves of figure 1, it is seen that the manner in which the conductance changes with increasing amounts of sodium silicate varies widely with the initial conductivity of the water. The higher the initial conductivity, the greater is the total lowering of the conductance and the more sodium silicate required to cause the maximum depression. A comparison of these curves with those of hydrochloric acid (figure 2) and sodium hydroxide (figure 3) shows quite definitely that the main impurity in the water is acidic in nature and without doubt is carbonic acid. The conductance of water of lower conductivity than 0.5×10^{-6} is seen to rise continuously, thus showing that either there is no carbon dioxide present below this

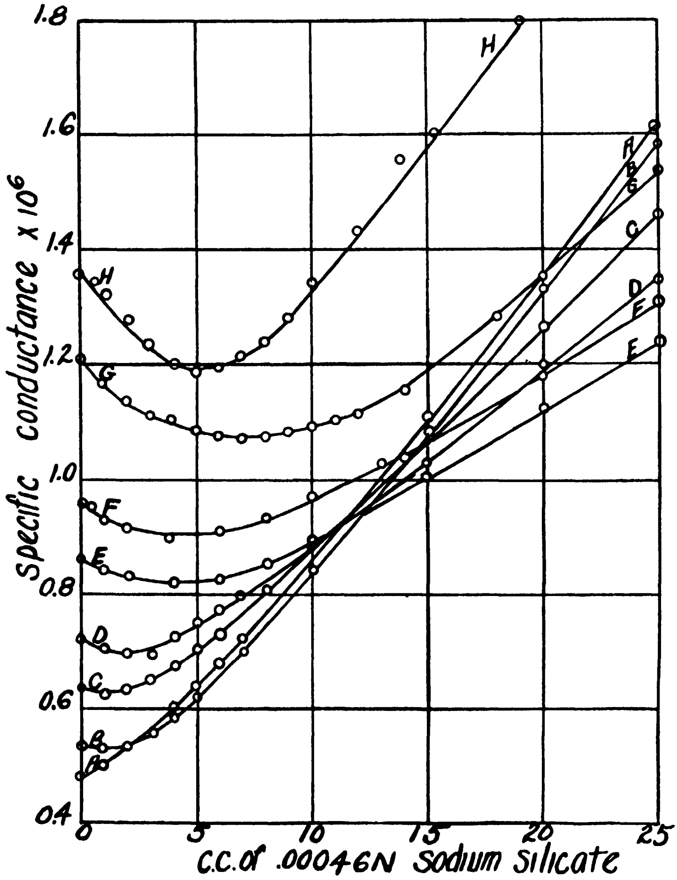


FIG. 1. EFFECT OF SODIUM SILICATE ON THE CONDUCTANCE OF CONDUCTIVITY WATER OF VARYING INITIAL SPECIFIC CONDUCTIVITIES

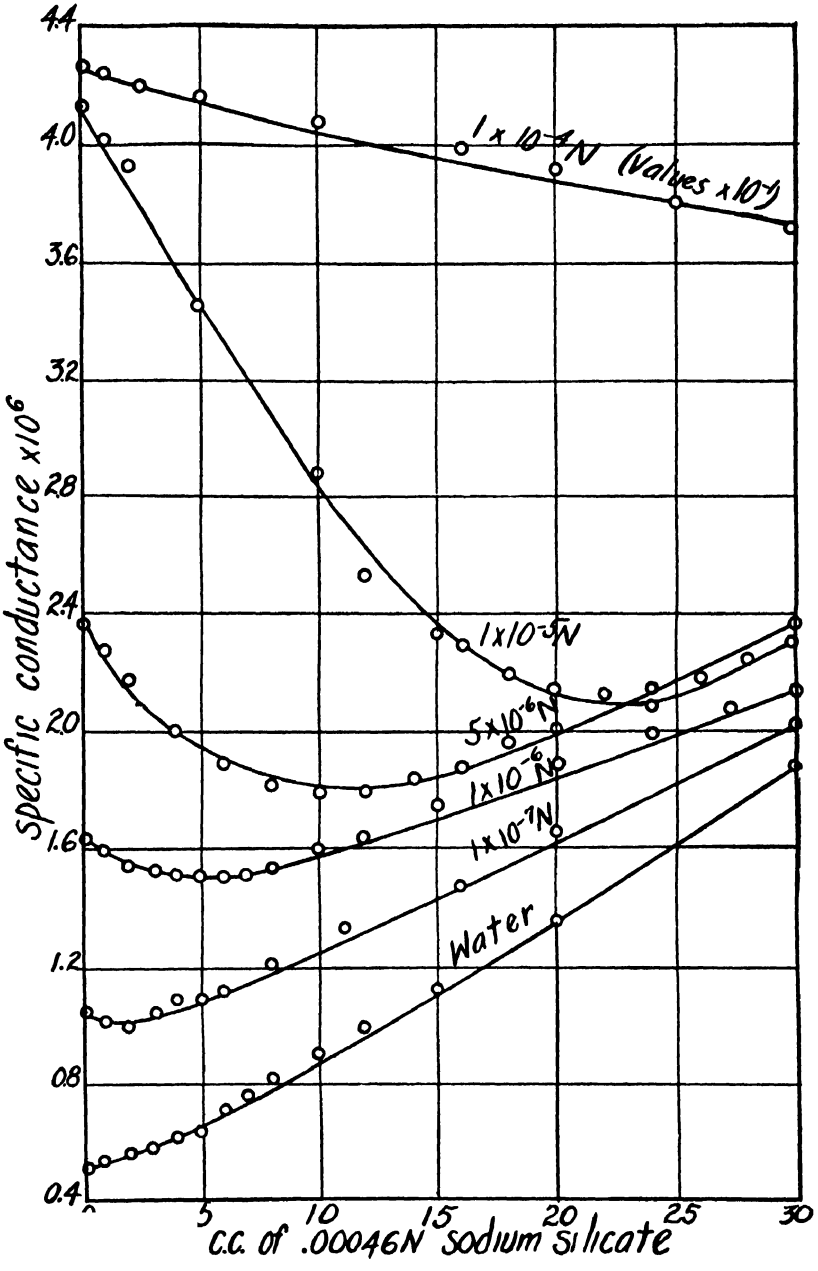


FIG. 2. EFFECT OF SODIUM SILICATE ON CONDUCTANCE OF HYDROCHLORIC ACID SOLUTIONS

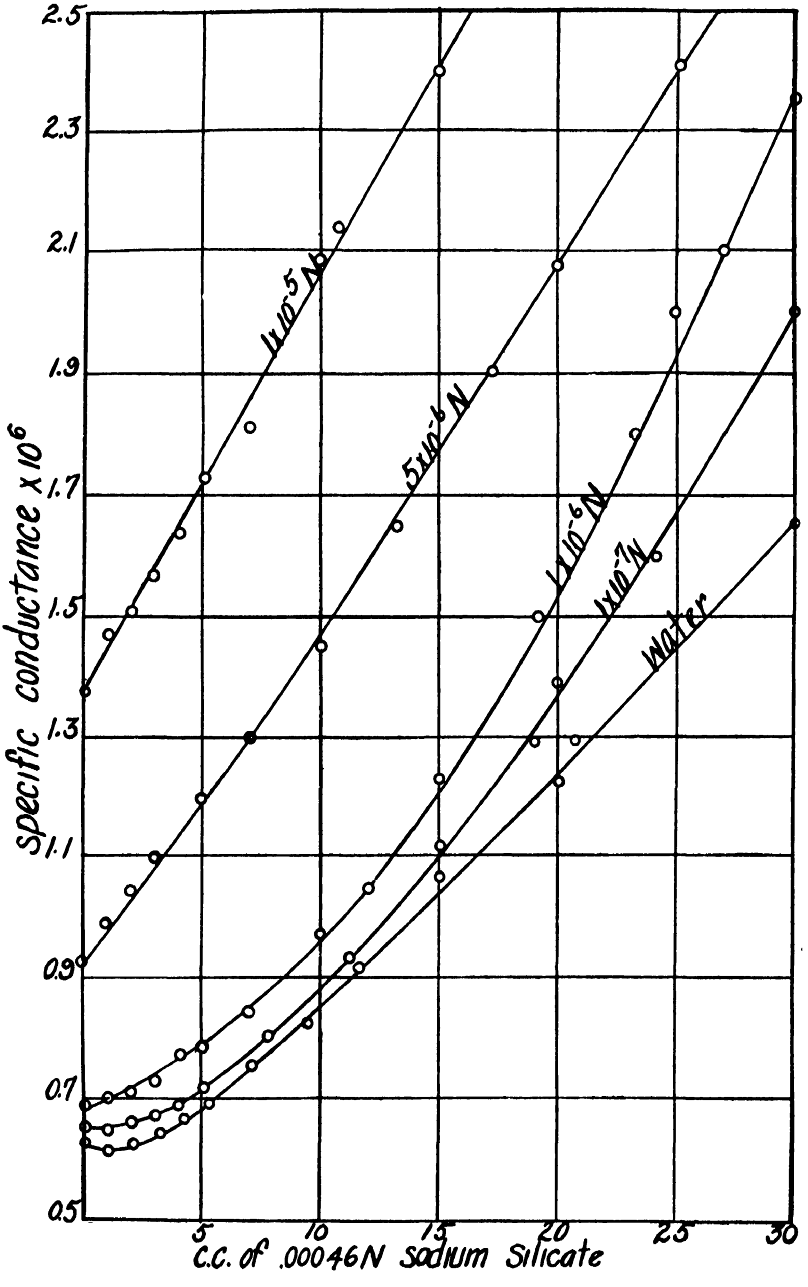


Fig. 3. Effect of Sodium Silicate on Conductance of Sodium Hydroxide Solutions

value, or that all the carbon dioxide has been removed by reaction with sodium silicate dissolved from the Pyrex container while the water was being collected. The latter is probably the case. It is seen from these curves that a "carbonic acid" solvent correction cannot be applied to water below

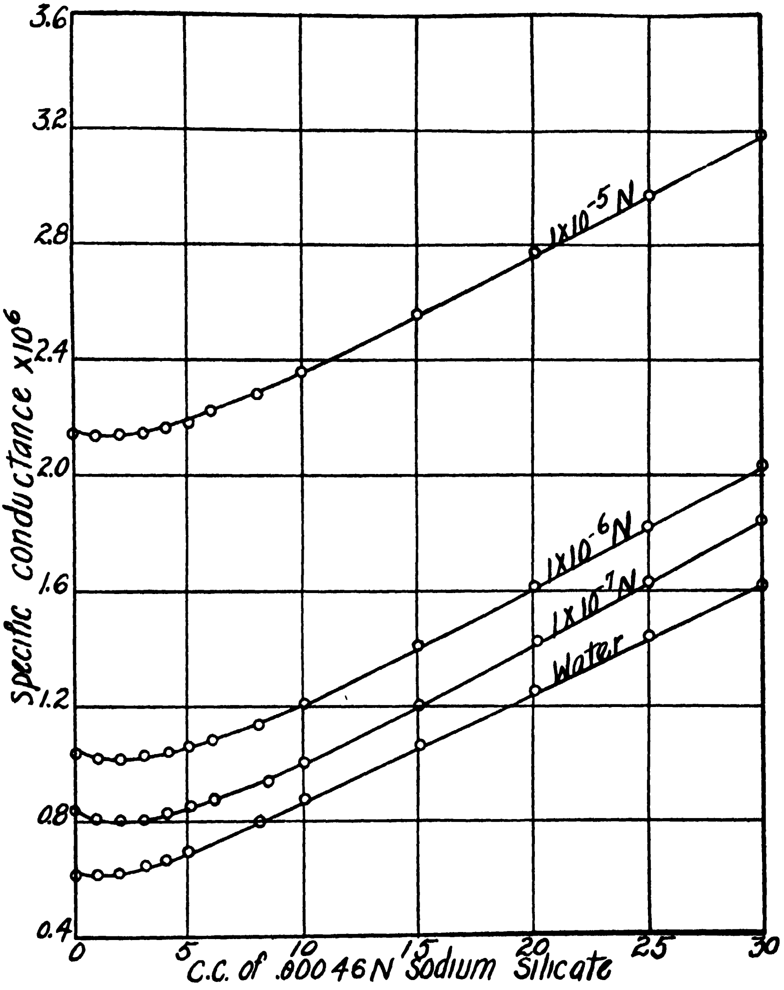


Fig. 4. Effect of Sodium Silicate on Conductance of Potassium Chloride Solutions

0.5 × 10^{-6} if it has been collected hot in Pyrex containers. The correction will rather be one for the "solution of glass," which involves a consideration of the products formed in the reaction of carbonic acid with silicates of sodium. For water of higher initial conductivity it is seen that the

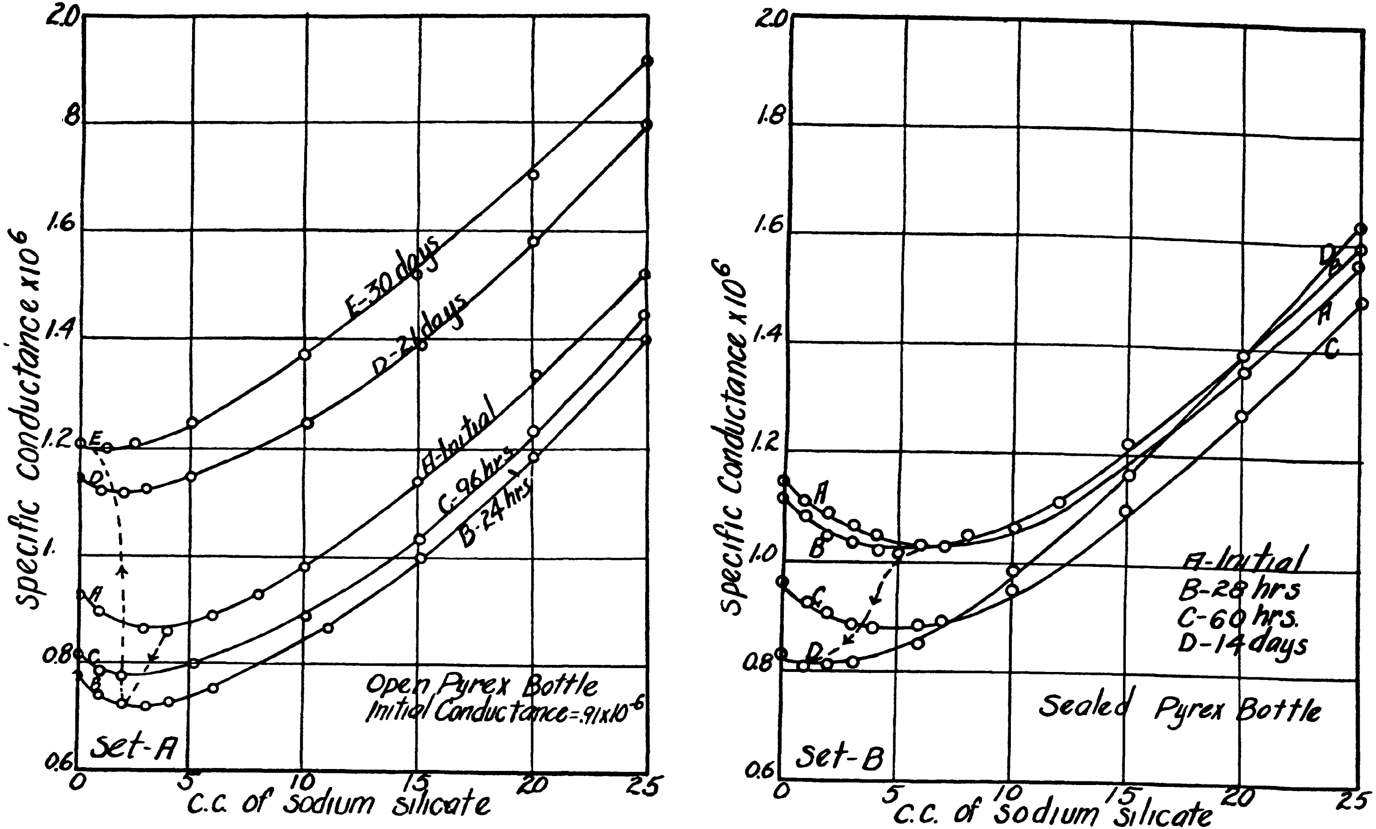


Fig. 5. Change of Carbon Dioxide Content of Conductivity Water with Time of Storage in Open and Closed Pyrex Bottles at 25°C.

correction will have to take into account both the carbon dioxide and the dissolved glass.

After the water has been collected, the relative amounts of carbon dioxide and dissolved silicates will vary with the time of storage. This is clearly shown by the curves of figures 5 and 6. The conductance of water in equilibrium with carbon dioxide of the air is 0.8×10^{-6}. The conductance of the water should tend toward this value, and the amount of sodium silicate required for maximum depression should be approximately 5 cc. (see figure 1) if no foreign substances interfered. From the curves it can be seen that the carbon dioxide is continually being removed, while the amount of dissolved glass increases. Thus with a Pyrex bottle, practically all the carbon dioxide has reacted with dissolved glass at the end of thirty

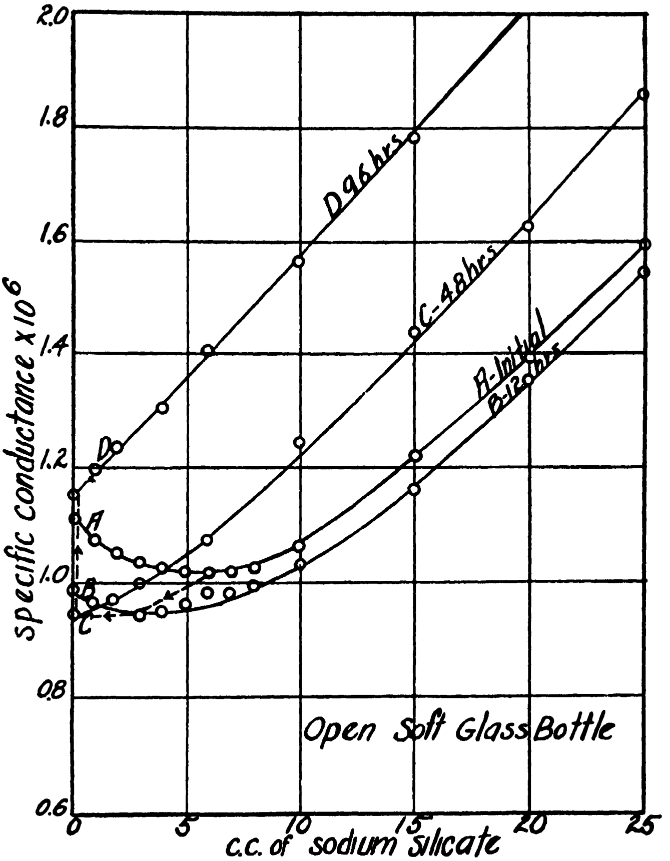


FIG. 6. CHANGE IN CARBON DIOXIDE CONTENT OF CONDUCTIVITY WATER WITH TIME OF STORAGE IN OPEN SOFT GLASS BOTTLES AT 25°C.

days and the conductance is now due to the products of the reaction. With soft glass the action is much faster. There is no carbonic acid present at the end of ninety-six hours. Water collected hot directly in a soft glass bottle showed no depression with sodium silicate solution, indicating the presence of no carbonic acid.

Parallel with these a bottle of water was stirred vigorously with a Pyrex glass stirrer. The time required for complete removal of carbon dioxide was forty-eight hours. Further experiments were run by bubbling hydrogen and nitrogen through the water. This had the effect of reducing the partial pressure of the carbon dioxide above the water, thereby decreasing the solubility of the carbon dioxide in the water; also it had the effect of increasing the rate of solution of the glass. Merely shaking the water in the flask gave a corresponding decrease in conductance. A summary of the results is given in table 1.

TABLE 1

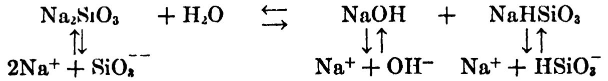
	TIME	INITIAL CONDUCTIVITY	FINAL CONDUCTIVITY
	hours		
Hydrogen	4	0.85×10^{-6}	0.47×10^{-6}
Nitrogen	4	0.96×10^{-6}	0.45×10^{-6}
Shaking	1	1.17×10^{-6}	0.93×10^{-6}

A direct measure of the solubility of Pyrex glass was attempted by evaporating in a platinum dish 10 liters of conductivity water which had been standing in a Pyrex bottle for fifteen months. The initial conductance was 1.0×10^{-6} and the final 1.23×10^{-6}. Conductometric titration with very dilute alkali showed that no carbon dioxide was present. The total solids obtained was 10.9 mg., of which 4.8 mg. was silica.

The need and application of a correction for this "solution of glass" in measuring the conductivity of very dilute solutions of electrolytes or even hydrogen-ion concentrations can clearly be seen from figures 2, 3, and 4. For strong acids a positive correction is needed, rather than the "normal" water correction or the zero correction assumed in the theory of the carbonic acid correction; for a basic solution a slight negative one is needed. The conductance of neutral salts is not affected abnormally by the presence of such small amounts of sodium silicate. The magnitude of the ideal correction could be determined by the solubility of the glass, the equilibrium relations with sodium carbonate, silicate, and bisilicate ions, and the mobilities of the ions involved. The uncertainty of the values and complexity of such calculations is at once evident when it is remembered they can be carried out only by a series of approximations. However, if the condition of the water is known, estimation of the approximate correction can be made with less difficulty.

From the laws of diffusion, it is known that if fresh conductivity water is put in a glass cell, the rate of solution or decomposition of glass will at first be comparatively large, owing to the high concentration gradient from the surface of the glass to the interior of the liquid. This gradient is maintained for a while by the effectual removal of the sodium silicate in the solution by reaction with the comparatively high concentration of carbonic acid. The complications and errors arising from the use of glass apparatus can easily be seen and one can see that water of 0.4×10^{-6}, or better, should be used if carbon dioxide can be excluded. If higher conducting water is to be stored some time before use, it might even be advisable to allow it to come to a carbonic acid-free condition (this can be determined by conductometric titration with dilute alkali), otherwise, worse complications set in because the relative amounts of carbon dioxide and silicates are not known exactly. The best way to eliminate such errors and complications if platinum is not available, is to use quartz, which is acted on only slightly by electrolytes and water, or wax-coated vessels for collection and storage of the water and solutions. Some of the newer types of bakelite preparations show some promise. A carbonic acid-free condition can nearly be obtained by bubbling nitrogen or hydrogen through until no further decrease in conductance is observed.

If, as was supposed by the earlier investigators, the sodium silicate is highly hydrolyzed in dilute solution to sodium hydroxide and colloidal silicic acid, one would expect the slope of the curves for sodium hydroxide to be less than the one for water, owing to depression of hydrolysis by the OH^- ion and to adsorption by the colloidal silicic acid. If, as suggested by Haag (7) the hydrolysis of the sodium metasilicate is represented as follows:



$$\begin{array}{cccccc} Na_2SiO_3 & + H_2O & \leftrightarrows & NaOH & + & NaHSiO_3 \\ \uparrow\downarrow & & & \downarrow\uparrow & & \downarrow\uparrow \\ 2Na^+ + SiO_3^{--} & & & Na^+ + OH^- & & Na^+ + HSiO_3^- \end{array}$$

then the limiting value of the hydrolysis will be 0.5. This can be assumed to be very nearly true, for it has been quite definitely demonstrated by Haag that practically all the silica in very dilute solutions of that ratio exists in the form of $HSiO_3^-$ ions and does not readily form colloidal particles. Since $NaHSiO_3$ is a highly ionized salt, the effect of such small OH^- ion concentrations in decreasing the hydrolysis is small, while its effect on the secondary ionization of silicic acid existing as hydrosilicate ions or crystalloidally is comparatively greater and the conductance will rise abnormally.

In the conductivity water, which can be considered a solution of carbonic acid, and in the hydrochloric acid solutions effectually what we have happening is an exchange of the slow-moving sodium ion for a fast-moving hydrogen ion, which results in a lowering of the conductance. This can be offered as an explanation of the maximum found in the data for very dilute solutions of strong acids.

If glass, as previously suggested, should be dissolved in the form of silicates of sodium, rich in silica, and practically all the silica is in the crystalloidal state as shown by Harman, then one can rightfully assume there is an equilibrium established between the crystalloidal silica, SiO_3^{--} ions, $HSiO_3^-$ ions, and the alkali. As an acid is added, an amount of SiO_3^{--} ions equivalent to the sodium hydroxide formed on hydrolysis plus half the sodium in the unhydrolyzed silicate is converted to $HSiO_3^-$ ions. On further addition these ions are converted to silicic acid which first separates out colloidally and then changes largely to the crystalloidal state. Thus it is seen that in making an ideal correction for the "solution of glass," one must take into account both the alkali and the silica, for even though, as Morey (12) has concluded from his isothermal saturation curves, there can be no true solubility of the silicate at ordinary temperatures, but rather a decomposition by the water, forming products which contain vanishingly small amounts of silica, the fact still remains that a large part of the substance dissolving is silica which furnishes silicate ions, bisilicate ions, and colloidal electrolyte. The excess silica may give rise to further complications owing to the formation of these colloidal electrolytes originally suggested by McBain (13) and more specifically applied to silicate solutions by Harman (8). Other substances undoubtedly dissolve which have their influence, but under conditions ordinarily met with in conductance or hydrogen-ion work, the solution of alkali and silica will be the greatest disturbing factor. Any reliable work carried out in glass apparatus on very dilute solutions, whether it be conductance, electrode potentials, or hydrogen-ion concentration, should take into consideration a correction for the "solution of glass."

SUMMARY

1. Measurements of the effect of small amounts of sodium silicate, such as are dissolved from glass, on the conductance of conductivity water of different initial conductivities and on very dilute solutions of hydrochloric acid, sodium hydroxide, and potassium chloride have been made.

2. The change in the nature of impurities in conductivity water with different methods of collection and time of storage in Pyrex and soft glass containers has been demonstrated.

3. It has been shown that in addition to a "normal" water correction, taking into consideration the carbonic acid present, there must also be applied a correction for the "solution of glass."

4. The correction for the "solution of glass" will depend upon the kind of glass used in storage and measurements of the conductivity water and the solutions, on the time of such storage and measurements, and on the nature of the electrolyte worked with. The magnitude of the ideal correction could be calculated from the ionic mobilities and equilibrium relations of

the substances formed by the interaction of the electrolyte with the carbonic acid, sodium carbonate, bisilicate, and crystalloidal silica found to be present. The approximate correction can best be obtained by taking into consideration the alkali, carbonates, and carbonic acid, the proportion of which can be approximately determined by conductometric titrations.

In conclusion I wish to express my thanks to Professors C. L. von Ende and J. A. Kostalek for the helpful suggestions offered and for placing the facilities of the Department at my disposal. The assistance and suggestions from the other members of the Department is also appreciated.

REFERENCES

(1) KENDALL: J. Am. Chem. Soc. **38**, 1480, 2460 (1916); **39**, 7 (1917).
(2) WASHBURN: J. Am. Chem. Soc. **40**, 106 (1918).
(3) WHETHAM AND PAINE: Proc. Roy. Soc. London **A81**, 58 (1908).
(4) WYNNE-JONES: J. Phys. Chem **31**, 1651 (1927).
(5) FORESTER: Z. anal. Chem. **33**, 381 (1894).
(6) WALKER: J. Am. Chem. Soc. **27**, 865 (1905).
WALKER AND SMITHER: Bur. Standards, Technol. Paper 107 (1918).
(7) HAAG: Z. anorg. allgem. Chem. **156**, 21 (1926).
(8) HARMAN: J. Phys. Chem. **32**, 44 (1928).
(9) HALL AND ADAMS: J. Am. Chem. Soc. **41**, 1515 (1919).
(10) WAGNER: Elektrotech. Z. **32**, 1001 (1911).
(11) SHEDLOVSKY: J. Am. Chem. Soc. **54**, 1411 (1932).
(12) MOREY: J. Glass Tech. **6**, 20 (1922).
(13) MCBAIN AND SOLMON: J. Am. Chem. Soc. **42**, 426 (1920).

THE DISTRIBUTION OF METHYLAMINE BETWEEN WATER AND CHLOROFORM AND THE EXISTENCE OF METHYLAMINE COMPLEXES OF THE METAL-AMMINE TYPE

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OBJECT OF THE INVESTIGATION

The purpose of this investigation was the determination of the ratio of distribution of monomethylamine between water and chloroform and the presentation of evidence for the existence and composition of its complex with a copper salt.

The existence and constitution of complexes of ammonia with salts have been shown in many cases; an excellent summary has been given by Miss M. M. J. Sutherland (1). There is some evidence that amines form complexes similar to these ammines, though very few data are recorded in the literature. E. Thiele (2) found that copper oxide dissolved in aqueous monomethylamine solution to form a solvent for cellulose. Von Euler (3) found that silver salts and methylamine react to form the complex ion $[Ag(CH_3NH_2)_2]^+$, having a dissociation constant at 25°C. of 2.45×10^{-7}. Wuth (4) came to a somewhat different conclusion of this same complex, as a solid, from his solubility investigations of silver chloride and bromide in methylamine solution. Olmer (5) has determined the solubility of silver oxide in aqueous methylamine.

One of the most direct determinations of the constitution of ammines in solution is furnished by the application of the distribution law. Nernst (6) pointed out that a constancy in the distribution ratio can exist only between those molecules of the distributed substance which are in the same molecular condition in the two phases. If the distributed molecules undergo reversible chemical combination, association, or dissociation, this effect must be taken into account before the constancy in the distribution can be detected. Conversely, it is clear that a knowledge of the distribution ratio could be used for the determination of the degree of chemical combination or of dissociation in either of the two phases. Moreover, if the distributed substance remains in the form of simple molecules in one phase and undergoes a change in the second phase, the extent of combination of the distributed substance with an added material in the second phase could be determined from the change in the distribution ratio caused by this added substance. Thus, Dawson and McCrae (7), by observing the change in the distribution ratio of ammonia between water and chloroform upon the addition of a definite amount of copper salt to the water, were able to show the existence of a complex ion containing four molecules of ammonia per atom of copper.

Applying this consideration to methylamine, if the distribution coefficient, uncorrected for any dissociation of methylamine in the water layer, is defined by the relation

$$P = C_1/C_2$$

for pure water, the relation for an aqueous salt solution (e.g., copper salt), becomes

$$P' = C_1'/C_2$$

where C_1' is the molal concentration of the methylamine in the aqueous salt solution and C_1 and C_2 are the molal concentrations in pure water and in chloroform, respectively. It follows that the amount of methylamine in the water layer uncombined with the copper salt and free to maintain the equilibrium with that in the chloroform layer will be given by the distribution coefficient for pure water at the corresponding concentration of methylamine in the chloroform layer, i.e., by

$$C_1 = C_2 \cdot P$$

while the remaining methylamine, that is, the amount combined with the copper salt, is given by

$$C_1' - C_1 \text{ or } C_1' - C_2 \cdot P$$

Hence, if C_x is the concentration of copper ion in the water, the number of molecules of methylamine combined with one copper ion will be given by the relation

$$\frac{C_1' - C_1}{C_x}$$

In assuming that the concentration C_1 calculated by this method is the same as it would have been if no copper salt were present, it is necessary to presuppose that the addition of copper salt has *no* effect upon the respective physical properties of water and chloroform and that it is soluble only in the water phase.

It is also necessary to neglect the purely physical effect of the copper ions, the anions, or any complex ions formed upon the solubility of methylamine in water. If the concentration of these ions is small, the salting-out effect will be small, of course. Dawson and McCrae (8) studied the effect of a large number of salts upon the distribution of ammonia between water and chloroform; they came to the conclusion that the copper sulfate used in their distribution experiments decreased the solubility of ammonia in water. By analogy, it may be reasoned that it would have a similar salting-out effect upon the solubility of methylamine in water. In this investigation, the copper salt concentration is kept small, and hence the salting-out effect will be small; this effect has not been considered in making the calculations necessary to determine the constitution of the complexes formed.

THE DISTRIBUTION COEFFICIENT

Since the proposed method of investigation of the complexes requires an accurate knowledge of the distribution ratio of methylamine between water and chloroform, a search in the literature for this ratio was made. Smith (9) gives a value of 5.848 at 25°C. for the ratio C_1/C_2, as the mean of several determinations in which the methylamine concentrations in the water layer varied from 2.625 to 27.4 millimoles per liter. Moore and Winmill (10) give a value of 8.00 at 25°C. as the mean of two determinations in which the methylamine concentrations in the water layer were 0.1203 and 0.1312 gram-equivalents per liter. Both of these ratios were expressed in terms of volume concentrations.

The lack of agreement in the values of C_1/C_2 and the limited range of concentration over which the ratio has been determined made it necessary to determine accurately the ratio over a greatly extended concentration range before the composition of the ammine complexes could be determined.

Experimental procedure

The method consisted in analyzing both layers, after establishment of equilibrium, between an aqueous solution of methylamine and chloroform. Hantzsch and Sebaldt (11) have shown that such an equilibrium is quickly reached. A convenient volume of the aqueous methylamine solution, usually 150 cc., was placed with 200 cc. of chloroform in a Pyrex cylinder of approximately 500 cc. capacity. The cylinder was equipped with a ground glass stopper and two capillary stop-cocks, one sealed in near the bottom of the cylinder for the removal of the chloroform layer and one sealed in near the center for the removal of the water layer. The cylinder and contents were rotated in a water thermostat at 25° ± 0.01°C. for a period of four and one-half to six and one-half hours at a speed of sixteen to seventeen revolutions per minute.

After rotation, the cylinder was allowed to stand in an upright position in the thermostat for one and one-half hours to effect a separation of the layers. To eliminate loss of methylamine by evaporation, samples were forced by pressure of dry air into previously weighed glass-stoppered

Erlenmeyer flasks containing a known amount of standard sulfuric acid and, in the case of the chloroform layer analysis, enough distilled water to cover the chloroform layer. The flask and contents were weighed immediately. In the case of the water layer, it was possible to take a sample only slightly in excess of the amount required to neutralize the acid, the excess being subsequently titrated with 0.05 *M* or 0.005 *M* acid, depending upon the methylamine excess.

The method yielded reproducible results, indicating that no methylamine was lost by this procedure. In all determinations duplicate samples were taken from each layer, the aqueous samples weighing about 30 to 40 g. and the chloroform samples about 80 to 100 g. The total divergence from the mean for the samples from both layers was usually less than 0.1 per cent, the water layer yielding the most reproducible values. All titrations were made by weight, using methyl orange with the chloroform layer and methyl red with the aqueous layer. Methyl red is removed almost completely from water by chloroform in contact with it; hence methyl orange was used there.

Although Abbot and Bray (12) reported that an emulsion of water and chloroform can be broken up by slow rotation, it was found in this investigation that the turbidity refused to disappear even on long standing. To break up the emulsion, the samples were forced through two fine "fritted" glass filters in series with the discharge tubes. About 25 cc. of the equilibrium solutions was first forced through the filters and discarded before the sample for analysis was taken. Thus the filters could not alter the methylamine concentration of the sample proper.

Preparation of materials

The 0.5 and 0.05 *M* sulfuric acid solutions were prepared from C. P. sulfuric acid and standardized against 100 per cent sodium carbonate dried for two hours at 140°C. The usual precautions for highest accuracy were observed.

The 0.01 *M* sodium hydroxide was prepared from C. P. sodium hydroxide and standardized by weight against the 0.05 *M* sulfuric acid, using methyl red as an indicator.

The chloroform was Baker and Adamson quality chloroform, repurified by shaking with 10 per cent sodium hydroxide, washing three times with distilled water, shaking with 5 per cent sulfuric acid, washing again three times with distilled water, drying with a mixture of calcium oxide and calcium chloride, and then distilling. The distilled product was stored in well-stoppered dark bottles under an atmosphere of carbon dioxide to prevent oxidation. Samples kept thus for a week showed no effect on potassium iodide nor changed a color indicator. This observation is contrary to the observation of Dietrich (13).

Methylamine solutions were prepared by passing the gas into distilled water. The gas was liberated in an all-glass generator by the interaction of methylamine hydrochloride and concentrated sodium hydroxide solution. The methylamine hydrochloride was a purified product which, upon drying in a vacuum, had a melting point of 234°C. The final product gave *no* test for ammonia, dimethylamine, or trimethylamine.

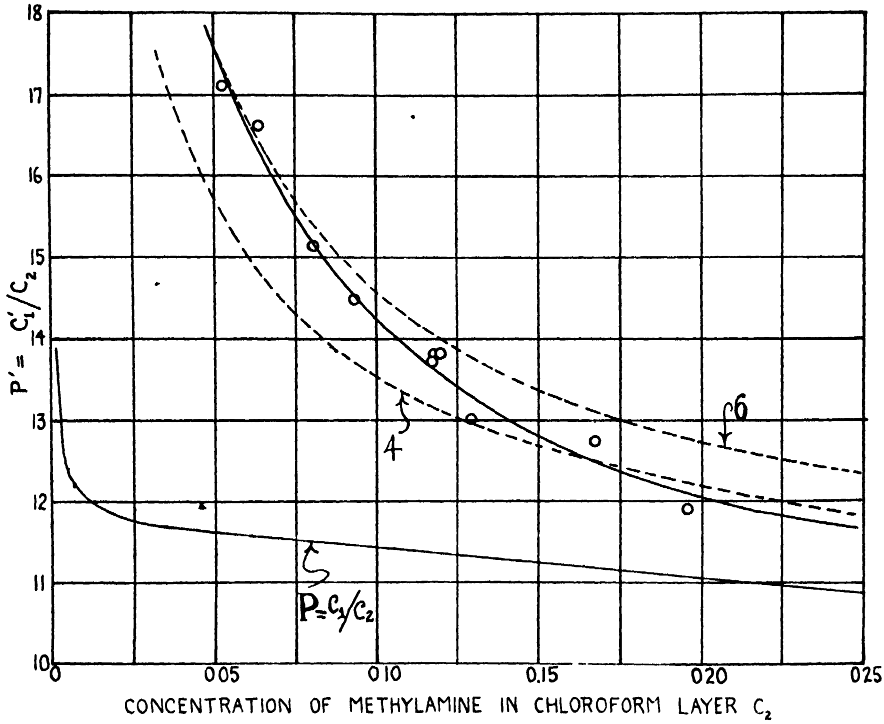

FIG. 1. DISTRIBUTION CURVE FOR METHYLAMINE BETWEEN 0.05 *M* COPPER SULFATE SOLUTION AND CHLOROFORM

EXPERIMENTAL RESULTS

The data and results of the distribution ratio determination are given in table 1. The last column contains the values of the true distribution ratio,[1] K_D, based upon calculations involving the dissociation of methylamine in water solution. The value of the dissociation constant, K_m, was taken as 4×10^{-4}, this being the most probable value derived from the published values of Bredig, of Bruni and Sandonnini, and of Harned and Benton (14).

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[1] $K_D = \dfrac{2C_1 + K_m \pm \sqrt{(K_m^2 + 4K_mC_1)}}{2C_2}$, where C_1 and C_2 are the molal concentrations of methylamine in the aqueous and the chloroform layers, respectively.

TABLE 1

Distribution of methylamine between water and chloroform

RUN	MOLALITY C_1 (water layer)	MOLALITY C_2 ($CHCl_3$ layer)	$P = C_1/C_2$	K_D
1	0 02113	0 001521	13 89	12 10
2	0 06876	0 005611	12 25	11 35
3	0 10151	0 008380	12 11	11 38
4	0 08601	0 007120	12 08	11 28
5	0 2003	0 01682	11 90	11 39
6	0 2484	0 02104	11 80	11 34
7	0 3793	0 03242	11 70	11 32
8	0 5837	0 05018	11 63	11 33
9	0 6850	0 05940	11 53	11 25
10	0 7917	0 06861	11 53	11 28
11	0 9741	0 08473	11 50	11 26
12	1 1157	0 09788	11 40	11 18
13	1 2773	0 1126	11 34	11 14
14	1 4714	0 1302	11 30	11 11
15	1 5563	0 1379	11 28	11 10
16	1 6858	0 1501	11 23	11 06
17	1 7485	0 1551	11 27	11 10
18	1 9960	0 1785	11 18	11 02
19	2 0384	0 1834	11 11	10 96
20	2 3779	0 2157	11 02	10 88
21	2 6180	0 2402	10 90	10 76

TABLE 2

Distribution of methylamine between aqueous copper sulfate solutions and chloroform

Concentration in molalities

RUN	C_1' (in $CuSO_4$ solution)	C (in $CHCl_3$)	P' (C_1'/C_2)	P (C_1/C_2)	C_1 (C_2 P)	C_x ($CuSO_4$)	$\frac{C_1' - C_1}{C_x}$
1	0 9037	0 05281	17 11	11 58	0 6115	0 0519	5 63
2	1 0523	0 06334	16 61	11 53	0 7303	0 0519	6 20
3	1 2238	0 08081	15 14	11 46	0 9261	0 0525	5 67
4	1 3494	0 09318	14 48	11 42	1 0641	0 0527	5 41
5	1 6093	0 1171	13 74	11 36	1 3302	0 0532	5 25
6	1 6238	0 1177	13 80	11 34	1 3347	0 0533	5 42
7	1 6547	0 1197	13 82	11 35	1 3586	0 0533	5 56
8	1 6793	0 1291	13 01	11 31	1 4601	0 0534	4 10
9	1 9322	0 1517	12 74	11 24	1 7051	0 0539	4 21
10	2 3399	0 1967	11 90	11 11	2 1853	0 0547	2 83

These values of K_D were plotted to large scale as functions of the concentration of methylamine in the chloroform layer. This dependency is given by the linear equation:

$$K_D = 11\ 39 - 2.32\ C_2$$

The variation shown is not explained by the distribution law; it is in accord, however, with the findings of Dawson and McCrae, of Bell and Fields, and of Occleshaw (15) on the distribution coefficient of ammonia between water and chloroform.

Complex formation with copper sulfate

Experimental procedure.—A stock solution approximately 0.5 molal in copper sulfate was prepared from carefully recrystallized salt. This solution, in any given determination, was diluted by adding to 15 g. of it exactly 150 g. of aqueous methylamine solution; this produced a solution approximately 0.05 molal in copper sulfate. Since part of the methylamine diffuses out of the water layer into the chloroform to establish equilibrium, the water layer loses weight by this amount. The actual concentration of copper sulfate in the water layer could be calculated from the known weight of aqueous solution and of chloroform placed together into the cylinder and the analytically determined distribution coefficient.

The two layers were analyzed as before with the same precautions. Methyl orange had to be used as indicator even with the water layer, because the copper hydroxide formed upon titration with acid masked the methyl red color change.

Experimental results.—The results of this series of determinations are presented in table 2. Since it was shown in table 1 that the uncorrected distribution coefficient for pure water and chloroform, $P = C_1/C_2$, varied with concentration of methylamine, it was necessary to ascertain the value of P corresponding to each concentration in the chloroform layer when the copper salt is present in the aqueous layer. This permits a calculation to be made of the concentration of the methylamine in the water layer which would exist if no salt were present and permits the calculation of the number of moles of methylamine in combination with the cupric ion. For this purpose the values of P from table 1 were plotted against the concentration, C_2, of methylamine in the chloroform layer. The values of P in column 4 of table 2 were taken from this curve. The last column of this table contains the calculated number of moles of methylamine combined per mole of copper sulfate; this ratio is not constant, *the value decreasing as the concentration of methylamine increases.* The data for copper sulfate are plotted in the accompanying figure; in addition there are included two other curves, shown dotted and marked 4 and 6, which represent the values of the distribution ratio that would be required if four and six molecules, respectively, of methylamine were united with one mole of copper sulfate (neglecting any other effect). An inspection reveals that the number of moles of combined methylamine per mole of copper sulfate *approaches six as a limit.* Since it would be extremely unusual for the cupric ion to combine with six moles of methylamine in a dilute solution and then liberate part of this in a more concentrated solution of the amine, it appears that the evidence supports the conclusion that methylamine is capable of uniting with the cupric ion in the ratio of 6 to 1 to form a complex ion with no indication that this complex dissociates appreciably even in dilute solution

SUMMARY

1 The distribution ratio of methylamine between water and chloroform has been determined over a range of concentrations in the water layer from 0 02113 to 2 6180 molal

2 The distribution ratio is not constant, except in the very dilute region (after correcting for dissociation), the ratio decreases with increasing concentration

3 Methylamine forms a complex of the ammine type with the cupric ion, the number of moles of methylamine to one cupric ion approaching *six* as a maximum The number in more concentrated methylamine solution *appears* to decrease

REFERENCES

(1) SUTHERLAND A Textbook of Inorganic Chemistry, Vol X (J N Friend, Editor-in-chief) J B Lippincott Co , Philadelphia (1928)
(2) THIELE, E Leipzig Farber-Ztg **56**, 56 (1907)
(3) VON EULER Ber **36**, 1854, 2878 (1903)
(4) WUTH Ber **35**, 2415 (1902)
(5) OLMER Bull soc chim **35**, 333 (1924)
(6) NERNST Z physik Chem **8**, 110 (1891)
(7) DAWSON AND MCCRAE J Chem Soc **77**, 1239 (1900)
(8) DAWSON AND MCCRAE J Chem Soc **79**, 493 (1901)
(9) SMITH, HOMER W J Phys Chem **25**, 626 (1921)
(10) MOORE AND WINMILL J Chem Soc **101**, 1662 (1912)
(11) HANTZSCH AND SEBALDT Z physik Chem **30**, 358 (1898)
(12) ABBOT AND BRAY J Am Chem Soc **31**, 729 (1909)
(13) DIETRICH J Phys Chem **33**, 95 (1929)
(14) BREDIG Z physik Chem **13**, 289 (1894)
BRUNI AND SANDONNINI Z Elektrochem **16**, 223 (1910)
HARNED AND BENTON J Am Chem Soc **52**, 5079 (1930)
(15) DAWSON AND MCCRAE J Chem Soc **89**, 1668 (1906)
BELL AND FIELDS J Am Chem Soc **33**, 940 (1911)
OCCLESHAW J Chem Soc **1931**, 1436

THE ACIDITY OF ORGANIC ACIDS IN METHYL AND ETHYL ALCOHOLS

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The investigation described in this paper was undertaken for the purpose of studying the changes in the acidity constants of certain organic acids as related (1) to changes in the character and position of substituted groups, and (2) to changes in the character of the solvent. The term acidity constant is used here in the same sense as it is defined by Brönsted (1). The methods employed in the study follow closely after those used by Michaelis and Mizutani (2). In short, it consists of measurements of the potential difference between a saturated potassium chloride calomel half-cell and a hydrogen electrode immersed in ethyl or methyl alcohol–water solutions of equimolecular concentrations of organic acids and their sodium salts. From such measurements the "reduced dissociation constants," as defined by Michaelis and Mizutani, or the equivalent values of K_A in Brönsted's equation

$$K_A = A_{\mathrm{H}^+} \cdot \frac{C_B}{C_A}$$

can be calculated. The activity of hydrogen ion, A_{H^+}, is assumed to be the same for two solutions of an acid, one in water and the other in alcohol or an alcohol–water mixture, when these show the same potential toward the normal hydrogen electrode. The limitations of this assumption, and of the method in general, are fully realized.

EXPERIMENTAL PROCEDURE

All materials were purified by the usual methods, and the usual precautions of E. M. F. measurements were observed. The Hildebrand bubbling electrode was used for all measurements of potential involving the hydrogen electrode. The electrodes were platinized lightly according to the directions of Popoff, Kunz, and Snow (3). Hydrogen was prepared by the electrolysis of a solution of sodium hydroxide. A Leeds and Northrup Type K potentiometer and Type R reflecting galvanometer were used in the determination of the potentials.

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[1] This paper was constructed from a thesis offered by William L. Bright in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Indiana University. Further details of the investigation are contained in the thesis, which was filed in the library of Indiana University, June, 1932.

A 0.1 *N* solution of the acid under consideration was prepared by dissolving the required amount of carefully weighed acid in absolute alcohol. The acid was weighed, using all the usual precautions and making the usual corrections, on a microanalytical balance. Flasks of 100 ml. capacity and carefully calibrated were used in making up these solutions. In making up the solutions of varying proportions of alcohol, 20 ml. of the 0.1 *N* acid solution and 10 ml. of a 0.1 *N* aqueous sodium hydroxide solution were added to a 100-ml. flask from a calibrated burette. The quantities of alcohol and water necessary to give the desired ratio of these solvents were then added.

The E. M. F. was read at five minute intervals, until two consecutive readings did not vary more than 0.2 millivolt. Equilibrium at the hydrogen electrode was usually reached in about twenty minutes. All measurements of E. M. F. were made in an air-bath at 25° (±1°)C. For the calculation of the pH of solutions, the values of the potential of the calomel half-cell at the temperature of the experiment have been taken from tables prepared by Clark (4). Other values used in calculating the pH of solutions for which the quinhydrone electrode was used were also obtained from Clark's tables.

In the few cases where our determinations overlap those made by Michaelis and Mizutani, we have been interested in checking our equipment and procedure against theirs. The two sets of values for the pH of the solutions are not quite in agreement, because it appears that Michaelis and Mizutani have used a different value for the E. M. F. of the saturated potassium chloride calomel half-cell than that given by Clark. Thus, at 18°C. Clark's value for this half-cell is 0.251 volt, while that used by Michaelis and Mizutani appears to be 0.2498 volt.

RESULTS

The results of the determinations are shown in table 1. The values of pH for solutions in 100 per cent alcohol are those obtained by extrapolation, an unavoidable method which is subject, of course, to some error. The points on the curve for zero per cent alcohol may be taken either from the observed pH values, or they may be based upon the convention, which is usually followed, that pK_A for aqueous solutions is equal to the pK of dissociation. Comparisons of the values obtained by the use of the quinhydrone and hydrogen electrodes have been made for the solutions of benzoic acid. The quinhydrone electrode was used in the study of the nitrobenzoic acids, since the hydrogen electrode did not give equilibrium readings in these solutions.

TABLE 1

Measurements of pH in alcohol–water mixtures

ALCOHOL PER CENT BY VOLUME	BENZOIC	BENZOIC (Quinhydrone)	o-TOLUIC	m-TOLUIC	p-TOLUIC	o-AMINOBENZOIC	m-AMINOBENZOIC	p-AMINOBENZOIC	o-HYDROXY-BENZOIC	m-HYDROXY-BENZOIC	p-HYDROXY-BENZOIC	o-CHLOROBENZOIC	m-CHLOROBENZOIC	p-CHLOROBENZOIC	o-NITROBENZOIC (Quinhydrone)	m-NITROBENZOIC (Quinhydrone)	p-NITROBENZOIC (Quinhydrone)	PROPIONIC	n-BUTYRIC	ISOBUTYRIC	n-VALERIC	ISOVALERIC	n-CAPROIC	ISOCAPROIC
Ethyl																								
0										4 04	4 51							4 68	4 83	4 77	4 74	4 65	4 80	4 75
20	4 48	4 48	4 32	4 62	4 84	5 28	4 97	5 23	3 33	4 54	4 97	3 42			2 63			5 23	5 24	5 29	5 41	5 24	5 20	5 22
40	5 31	5 13	5 21	5 37	5 46	5 87	5 49	6 06	3 73	5 24	5 72	4 22	4 79		2 77	3 60	3 95	5 86	5 84	5 94	6 05	5 90	5 83	5 94
50	5 64	5 44	5 61	5 72	5 80	6 20	5 83	6 43	4 01	5 61	6 07	4 55	5 11	5 20	3 59	4 32	4 15	6 16	6 18	6 33	6 39	6 24	6 21	6 28
70	6 24	6 03	6 32	6 40	6 36	6 90	6 52	7 19	4 62	6 36	6 80	5 18	5 72	5 81	4 20	4 85	4 69	6 80	6 83	7 00	7 03	6 87	6 85	6 95
80	6 61	6 30	6 67	6 75	6 73	7 29		7 60	4 90	6 73	7 23	5 51	6 06	6 13	4 52	5 17	5 00	7 19	7 21	7 32	7 34	7 23	7 21	7 27
90	6 91	6 52	7 01	7 14	7 08	7 67		7 97	5 27	7 11	7 66	5 82	6 39	6 49	4 85	5 43	5 28	7 56	7 56	7 70	7 65	7 57	7 53	7 63
95		6 92		7 32	7 32	7 84		8 16	5 46	7 30	7 88	5 98	6 54	6 69	4 98	5 57	5 47	7 76	7 74	7 90	7 76	7 74	7 71	7 81
100*	7 29	7 10	7 34	7 50	7 36	8 00	7 54	8 38	5 61	7 48	8 10	6 14	6 70	6 84	5 14	5 70	5 54	7 96	7 90	8 08	7 98	7 92	7 88	7 98
Methyl																								
20	4 41											3 20			2 70	3 56		5 19	5 14	5 54	5 29	5 15	5 19	5 14
40	4 92											3 78	4 37		3 01	3 86		5 64	5 61	5 97	5 79	5.64	5 66	5 62
50	5 15											4 02	4 70		3 16	4 04	4 16	5 84	5 88	6 23	6 04	5 89	5 91	5 90
70	5 72											4 63	5 26	5 55	3 70	4 46	4 51	6 41	6 41	6 70	6 54	6 41	6 44	6 40
80	5 97											4 94	5 56	5 74	3 83	4 68	4 74	6 68	6 64	6 96	6 83	6 68	6 64	6 61
90	6 12											5 20	5 77	5 91	4 25	4 81	4 97	6 94	6 96	7 17	7 09	6 92	6 85	6 93
95	6 37											5 31	5 90			5 01	5 12	7 06	7 09		7 19	7 04	7 13	7 04
100*	6 50											5 48	6 02	6 14	4 52	5 12	5 20	7 20	7 24	7 40	7 33	7 29	7 26	7 16

* Extrapolated. All measurements are by hydrogen electrodes except where quinhydrone is indicated.

DISCUSSION OF RESULTS

Variations of K_A with differences in the structure of the acids

The acidity constants of the substituted benzoic acids show the effect of (1) the nature of the substituent, and (2) its position in the benzene nucleus with respect to the carboxyl group. We may interpret these effects in the light of Kharasch's (5) measurements of the relative electronegativities of different organic radicals. Accepting his meaning of the term electronegativity, it appears that the more electronegative the atom or group (R) attached to the hydroxyl radical (ROH), the more readily hydrogen is removed from its linkage with oxygen; thus, phenol is a stronger acid than methyl alcohol. In keeping with the interpretation

TABLE 2

*The acidity constants of substituted benzoic acids in methyl and ethyl alcohols**

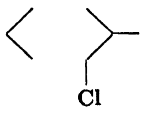
I ACID	II pK_A†	III $pK_A - pK_A$(Benzoic acid)
Ethyl alcohol		
o-Nitrobenzoic	5.14	−2.15
p-Nitrobenzoic.	5.54	−1.75
Salicylic	5.61	−1.68
m-Nitrobenzoic	5.70	−1.59
o-Chlorobenzoic	6.14	−1.15
m-Chlorobenzoic	6.70	−0.59
p-Chlorobenzoic	6.84	−0.45
Benzoic. .	7.29	0.00
o-Toluic.	7.34	0.05
p-Toluic	7.36	0.07
m-Hydroxybenzoic	7.48	0.19
m-Toluic. .	7.50	0.21
m-Aminobenzoic	7.54	0.25
o-Aminobenzoic	8.00	0.71
p-Hydroxybenzoic	8.10	0.81
p-Aminobenzoic	8.38	1.09
Methyl alcohol		
o-Nitrobenzoic	4.52	−1.98
m-Nitrobenzoic	5.12	−1.38
p-Nitrobenzoic	5.20	−1.30
o-Chlorobenzoic	5.48	−1.02
m-Chlorobenzoic	6.02	−0.48
p-Chlorobenzoic	6.10	−0.40
Benzoic . .	6.50	0.00

* The acids are listed in the order of decreasing acidity.

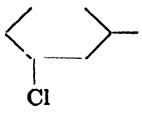
† Uncorrected for ion activity instead of ion concentration.

below, this may mean that the presence of the electronegative atom or group causes oxygen (in OH) to act less electronegatively toward hydrogen and, therefore, to hold hydrogen less firmly. Concerning substitutions for hydrogen in the radical R, Kharasch finds that the more electronegative the substituent, the less readily this radical combines with hydrogen. He takes this to mean that R becomes less electronegative (toward hydrogen). The acidity constants of the substituted benzoic acids indicate that the more electronegative the substituent, the more readily hydrogen can be removed from its linkage with the RCOO— group. To apply Kharasch's reasoning to these results, it appears that we must assume that the substitution of an electronegative atom or group in R causes the RCOO— group to act less electronegatively toward hydrogen. There is the other view, of course, that the electronegative substituent causes the RCOO— group to act *more* electronegatively toward hydrogen. The increase in the strength of the acid may be due, in other words, to a change in the RCOO—H linkage which makes it more electrovalent and less covalent in character. Our present purposes do not require a discussion of the merits of these two points of view.

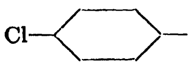
Kharasch finds that the presence of chlorine in any position in the phenyl group causes this group to exert a slightly decreased electronegativity toward any atom or group attached to it. This we may call the *primary* effect. This primary effect is modified somewhat by a *secondary* effect, which depends upon whether chlorine occupies the ortho, meta, or para position. The latter may be due to the orienting effect of chlorine upon the six "aromatic" electrons to which benzene owes its unsaturation.



Increased electronegativity



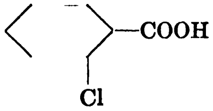
Decreased electronegativity



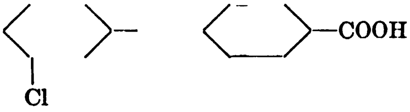
Increased electronegativity

Accordingly, chlorine in the meta position still further decreases the electronegativity of phenyl. Para and ortho chlorine, on the other hand, oppose the primary effect of the substitution of chlorine and slightly increase the electronegativity of the radical, although they do not overcome the decrease produced by the primary effect of chlorine. According to Kharasch's findings, the electronegativity of *p*-chlorophenyl is greater than the electronegativity of *o*-chlorophenyl; and both radicals are more electronegative than *m*-chlorophenyl. Chlorine in the para position acts, therefore, as a slightly less electronegative substituent than meta chlorine. Hence, *p*-chlorobenzoic acid should possess a smaller acidity constant than *m*-chlorobenzoic acid, in which both the primary and secondary effects act in the same direction. The acidity constant of *p*-chlorobenzoic acid falls next above that of benzoic acid. It appears, therefore, that in *p*-chlorobenzoic acid the secondary effect of chlorine in the para position almost neutralizes the primary effect.

The order of the acidity constant of *o*-chlorobenzoic acid is not what we might expect. Based upon Kharasch's order of electronegativity we should predict that *o*-chlorobenzoic acid should be intermediate, but instead it is stronger than either *p*-chlorobenzoic or *m*-chlorobenzoic acid. This discrepancy may be due to several causes. In the substituted benzoic acids, hydrogen is attached to an oxygen atom of the carboxyl group, which is itself a substituent in the phenyl group. If the carboxyl group is *very weakly* electronegative, as Kharasch believes, its effect is opposite to that of chlorine. For certain positions of chlorine the effects of the two substituents may be such as to decrease the electronegativity of phenyl toward chlorine. In such cases we must consider the electronegativity of chlorine toward phenyl as having been increased. In *o*-chlorobenzoic acid both chlorine and carboxyl may orient the six aromatic electrons of phenyl to the same positions:



The increased electronegativity of chlorine in the ortho position results in slightly increased strength for *o*-chlorobenzoic acid. In *m*-chlorobenzoic acid the orienting influences of carboxyl and chlorine are opposed:



In this case carboxyl slightly decreases the electronegativity of chlorine toward phenyl. This makes *m*-chlorobenzoic acid weaker than *o*-chlorobenzoic acid.

Methyl is less electronegative than chlorine. The tolyls are correspondingly more electronegative than the chlorophenyls. The toluic acids are weaker than benzoic. Their acidity constants fall in the order $o > p > m$. The order of the electronegativity of the tolyls is the same. Methyl in the ortho and para positions, as in the case of the substitution of chlorine, appears to increase slightly the electronegativity of phenyl. Since the primary effect of methyl-substitution also results in an increase in electronegativity, the two effects are additive in the *o*- and *p*-tolyls. Methyl in the meta position, however, slightly decreases the primary effect. Hence, *o*- and *p*-tolyl are more electronegative than *m*-tolyl.

Carboxyl should slightly increase the electronegativity of ortho or para methyl and decrease that of meta methyl. These differences in the electronegativity of methyl in its different positions account for the order of acidity constants.

The order of the acidity constants of the nitrobenzoic acids in ethyl alcohol is $o > p > m$. We cannot be certain of the order of the electronegativity of the nitrophenyls. The nitro group is more electronegative than chlorine; the nitrobenzoic acids are correspondingly stronger than the chlorobenzoic acids. If the hydroxyl radical has the same effect as methyl upon the electronegativity of the phenyl group, hydroxybenzoic acids should be weaker than benzoic acid. Kharasch states that both groups increase the electronegativity of phenyl, but he does not state that this is true for all positions of the hydroxyl radical. We find *o*-hydroxybenzoic (salicylic) acid stronger than benzoic acid, while the meta and para acids are weaker. In the hydroxybenzoic acids two hydroxyl groups are present, one in each substituent. The effect of the presence of these two groups on adjacent carbon atoms may have a profound influence upon the acidity constant of *o*-hydroxybenzoic acid. This effect may be of the same character as that which a hydroxylic solvent, such as water, exerts upon the dissociation of an acid dissolved in it.

The acidity constants of the aminobenzoic acids in ethyl alcohol are in the order $m > o > p$. This indicates that the amino radical has the opposite effect of chlorine and methyl upon the orientation of the "aromatic" electrons of phenyl. If the substitution of the amino group increases the electronegativity of phenyl, then the secondary effects of amino in the meta position will cause phenyl to be still more electronegative. Substitution of the amino radical in the ortho and para positions, however, will tend to decrease the electronegativity of phenyl. If this reasoning is correct, the order of electronegativity of the aminophenyls should be $m >$ (o and p). If the amino group is less electronegative than carboxyl, as seems likely, then the effect of carboxyl will be to make the ortho and para amino groups slightly less and the meta amino radical slightly more negative than when carboxyl is not present. These differences should make *m*-aminobenzoic acid slightly stronger than *o*- and *p*-aminobenzoic acids. The whole question of the acidity constants of the aminobenzoic acids, however, must be considered in the light of their amphoteric character.

The order of the acidity constants of the acids in methyl alcohol is the same as in ethyl alcohol. The acidity constants of the aliphatic acids (table 3) show no differences of any significance in either methyl or ethyl alcohol.

Variations of acidity constants of acids in water, methyl alcohol, and ethyl alcohol

The effect of the change of solvent upon the acidity constants of different acids (table 3) is not constant, and does not depend entirely upon the dielectric constants of the solvents. The change in K_A with change of medium is determined by the effect of the medium upon the ratio f_A/f_B of the activity coefficients of the uncharged acid and its anion. For monobasic organic acids, such as those which we have studied, the change from a medium of high to one of low dielectric constant should cause a slight decrease in the activity coefficient of the undissociated acid and an increase in the activity coefficient of the monovalent anion of the acid. These effects should result in a decrease in the acidity constant or an increase

TABLE 3

Changes of pK_A of acids with changes of solvent*

I ACID	II pK_A IN C_2H_5OH	III pK_A IN CH_3OH	IV pK_A† IN WATER	V pK_A II − IV	VI pK_A III − IV	VII pK_A II − III
o-Nitrobenzoic.	5 14	4 52	2 63‡	2 51	1 89	0 62
p-Nitrobenzoic .	5 54	5 20	3 40	2 14	1 73	0 34
Salicylic	5 61		2 97	2 64		
m-Nitrobenzoic	5 70	5 12	3 46	2 24	1 66	0 58
o-Chlorobenzoic .	6 14	5 48	2 88	3 26	2 60	0 66
m-Chlorobenzoic	6 70	6 02	3 81	2 89	2 21	0 68
p-Chlorobenzoic	6 84	6 10	4 04	2 80	2 06	0 74
Benzoic.	7 29	6 50	4 18	3 11	2 32	0 79
o-Toluic	7 34		3 90	3 44		
p-Toluic	7 36		4 37	2 99		
m-Hydroxybenzoic	7 48		4 08	3 40		
m-Toluic.	7 50		4 25	3 25		
m-Aminobenzoic	7 54		4 79	2 75		
o-Aminobenzoic	8 00		4 97	3 03		
p-Hydroxybenzoic	8 10		4 54	3 56		
p-Aminobenzoic	8 38		4 92	3 46		
Propionic	7 96	7 20	4 88	3 08	2 32	0 76
n-Butyric	7 90	7 24	4 82	3 08	2 42	0 66
Isobutyric	8 08	7 40	4 81	3 27	2 59	0 68
n-Valeric	7 98	7 33	4 81	3 17	2 52	0 65
Isovaleric	7 92	7 29	4 77	3 15	2 52	0 63
n-Caproic .	7 88	7 26	4 85	3 03	2 41	0 62
Isocaproic	7 98	7 16	4 84	3 14	2 32	0 82
Average				3 02	2 25	0 65

* Uncorrected for ion activities instead of ion concentration

† $pK_A = pK_{Diss}$ for aqueous solutions

‡ By graphical extrapolation.

in the values of pK_A. This is true for all the acids studied. The change in the acidity constants of the aliphatic acids (from one medium to another) is practically constant. But for the substituted benzoic acids the change of pK_A with change of medium is decidedly different for the different acids. In general it may be said that the change in pK_A increases with decreasing acidity. For those acids which are stronger than benzoic acid, the change in pK_A is less than for benzoic acid. For those which are weaker than benzoic acid, the change in pK_A is somewhat greater than or approximately the same as for benzoic acid. Even for the chain acids, a slight increase of the change is to be noted as the acidity decreases. In some cases (the hydroxybenzoic acids for example) there is a wide variation in the extent of the change of pK_A for the ortho, meta, and para isomers. In other cases, notably in the cases of the toluic acids, the effect is about the same for all three forms.

The relative order of the acidity constants of the different acids in ethyl alcohol, methyl alcohol, and water is not the same. This indicates that the effects, such as solvation, etc., upon the ratio of the activity coefficients of the acid and its anion in the three solvents are not comparable except for very closely related acids, such as those of the aliphatic series.

The difference between the negative logarithms of the basicity constants of water and ethyl alcohol can be measured by determining the difference between the negative logarithm of the dissociation constant of an acid in alcohol and the negative logarithm of the acidity constant of the same acid in alcohol. Kolthoff (8) has calculated this difference for salicylic and benzoic acids. His values are based upon the acidity constants of Michaelis and Mizutani, which he corrects for ion activities in place of ion concentrations. Using a similar method of calculation, our determinations for the three nitrobenzoic acids show a practically constant difference of 2.86 logarithmic units. This value is slightly higher than that obtained for salicylic and benzoic acids, in which cases our average difference was 2.7 logarithmic units. The latter figure is in agreement with Kolthoff's calculations. For the dissociation constants of the acids in ethyl alcohol and water we have used the data of Larsson (9), Goldschmidt (10), and Bjerrum and Larsson (11).

The determinations of the pK_A values for the nitrobenzoic acids were made, necessarily, by means of the quinhydrone electrode. We have measured the acidity constant of benzoic acid in water–alcohol mixtures by means of both hydrogen and quinhydrone electrodes. These results show a greater value for pK_A when the determination is carried out by means of a quinhydrone electrode than when the same value is measured by the hydrogen electrode. For the smaller concentrations of alcohol the differences in the two determinations of pK_A are negligible. But the extrapolated values of pK_A in 100 per cent alcohol show a difference of

0.19 logarithmic unit. Two similar determinations were also made of the pK_A of *p*-toluic acid; the difference between these was 0.15 unit. If we assume that the difference is of the same order for the nitrobenzoic acids, then the difference between the negative logarithms of the basicity constants of ethyl alcohol and water is $2.86 - 0.17 = 2.69$, which is the same value as we have found for the solutions of benzoic and salicylic acids.

The determinations of the relative basicity constants of different solvents are largely dependent upon accurate determinations of the dissociation constants of the acids dissolved in such solvents. Available data do not permit the determination of a single value for the difference between the negative logarithms of the basicity constants of water and methyl alcohol. So far, the determinations in ethyl alcohol are limited to five solutions, three of which are discussed in this paper for the first time.

REFERENCES

(1) BRÖNSTED: Chem. Rev. **5**, 231 (1928).
(2) MICHAELIS AND MIZUTANI. Z. physik. Chem. **116**, 135 (1925).
(3) POPOFF, KUNZ, AND SNOW: J.Phys. Chem. **32**, 1056 (1928).
(4) CLARK: The Determination of Hydrogen Ions, 3rd ed., p. 672. The Williams & Wilkins Co., Baltimore (1928).
(5) KHARASCH AND REINMUTH: J. Chem. Education **5**, 404 (1928); **8**, 1703 (1931). KHARASCH AND FLENNER: J. Am. Chem. Soc. **54**, 674 (1932).
(6) KOLTHOFF: J. Phys. Chem. **36**, 2732 (1932).
(7) LARSSON: Z. physik. Chem. **148**, 148 (1930).
(8) GOLDSCHMIDT: Z. physik. Chem. **99**, 116 (1921).
(9) BJERRUM AND LARSSON: Z. physik. Chem. **127**, 358 (1927).

THE PHYSICAL CHEMISTRY OF FLOTATION. II

THE NATURE OF THE ADSORPTION OF THE SOLUBLE COLLECTORS

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It having been demonstrated that the angle of contact plays a very important part in determining the tenacity of attachment between a conditioned mineral surface and air, it becomes important to determine what factors determine the angle of contact. The magnitude of the angle of contact is fixed by the interfacial tensions of the three phases meeting at the line of triple contact mineral–air–water. Consequently, any factor having an effect on any one of the three surface tensions (or surface energies) will influence the angle of contact.

Every surface change may be expected to influence the surface energy, and thus no factor which influences the surface is without influence on flotation. Confusion has arisen in the literature owing to a lack of appreciation of this fact. Thus several writers, in emphasizing the importance of some one factor, have put forward their views as a complete theory of flotation. Even the writers of textbooks refer to the "contact angle theory of flotation," the "adsorption theory of flotation," etc.

Though no one factor is responsible for flotation, no factor is more important in flotation by soluble collectors than adsorption, and this is particularly true of adsorption at the solid surface. It has been shown (1) that air does not even partially replace water from clean surfaces of many common sulfide or gangue minerals. Metals and oxidized minerals behave similarly. It is only after the surfaces have acquired a coating of some "collector" that any displacement of water by air is possible at the surface. In the early application of flotation, the collectors used were oils and the surfaces were filmed by oil. Latterly, oils have been largely displaced as collectors by soluble non-oleaginous compounds, of which potassium ethyl xanthate is the most used. These, only, are considered in the present discussion. Under certain conditions unimolecular films are adsorbed by the minerals which then display a definite air avidity.

The orientation of the adsorbed molecule is all-important. If there be no polar group in the surface, contact with air (and displacement of water) is possible; if there be a polar group in the surface, contact with air is impossible. The lead, zinc, and copper salts of mandelic acid float very readily, though they are heavier than water. Mandelic acid contains two active groups; it is evident that both are orientated inwards in these salts, which are coördination compounds, and that the non-polar phenyl group is orientated outwards. The parent acid and the sodium salt are not collectors, however, for the sulfide minerals, proving that if they are adsorbed, there is an active group outermost. Other acids might be cited whose heavy metal salts float readily but which, themselves, do not act as collectors for the sulfide minerals. On the other hand, it is probably true that an acid, or its soluble salts, would not cause floatability if the heavy metal salts were not themselves readily floatable.

There are three aspects of the adsorption of soluble collectors which need examination.

1. Under what conditions does adsorption of the collector occur?
2. At what rate does adsorption occur?
3. If adsorption occurs, how is the angle of contact related to the constitution of the collector?

The first question is the most difficult to answer. Modern selective flotation is based upon the adsorption of a collector by one mineral and not by another, and an explanation must be sought for the differences between minerals in this respect. It is avoiding the issue to say that certain minerals attract the CS·S— group, though this is the customary method of accounting for adsorption. Incidentally, a valid explanation for the adsorption of xanthates by minerals would mark an important step forward in the theory of adsorption.

Of the theories which have been advanced, none has received more attention than that which postulates that adsorption is due to the formation of an insoluble compound on the mineral surface, and attention should be drawn to certain exceptions, lest it be taken for granted that the theory is established. Of the other theories, that which seeks to explain adsorption in terms of surface charges is also worthy of more consideration, but in the absence of definite experimental verification we have perforce to confine our attention to the former, the so-called "chemical" theory.

The chemical theory has been sponsored by Taggart and Gaudin and their collaborators. Gaudin, Haynes, and Haas (2) state that it has appeared more and more as their experimental work has progressed that the action of reagents on the flotation of sphalerite is strictly chemical. Taggart, Taylor, and Knoll (3) advance the generalization, "Simple chemical reaction underlies the functioning of the flotation reagents which control mineral collection, when these reagents are soluble in and act from solution in the water of the pulp." The proviso excludes collectors which are oils. It was not claimed that this generalization was substantiated exhaustively, and we therefore propose to discuss its usefulness as a working hypothesis.

A truly chemical theory implies that adsorption can occur only when the solution is saturated with respect to the adsorbed compound. As early as 1915, Paneth and Horowitz (4) pointed out that the amount of adsorption of certain radioactive elements is dependent on the degree of insolubility of their salts. This conclusion was confirmed by Fajans and Horowitz (5).

Evidence has been adduced by Taggart and Gaudin and their collaborators to show that there is a close connection between adsorption of xanthate at a mineral surface and the solubility of the xanthate of the metal in the mineral. Before the chemical theory can be accepted, it must be shown that this connection amounts to identity. In other words, it is necessary to show that the forces controlling adsorption are of the primary valence type.

The adsorbed film is surprisingly stable. Once adsorption has occurred, contact with air continues to be possible though the surface be washed with several changes of water. The alkali metal xanthate of the solution from which adsorption has occurred is extremely soluble in water; the heavy metal salts are of extremely low solubility. The heavy metal xanthates, moreover, flocculate readily about an air bubble and then float readily. There is thus some presumptive but not conclusive evidence that the adsorption is due to an insoluble film of the heavy metal salt.

Taggart (3) has stated, "We are rather inclined to think that in every case the solubility of the substance as a surface coating is somewhat less than that of the same substance independently put into solution, but I do not know." The solubility term used in describing adsorption may thus be different from that of the solubility of the same compound in bulk. It is of significance that the statement quoted arose in a discussion following the presentation by Taggart and his associates of a paper in which an attempt was implicitly made to explain "adsorption" in terms of primary chemical reactions. Does it not amount to an admission that the explanation was incomplete, i.e., that secondary valences must be considered?

Gaudin, Haynes, and Haas (2) evidently doubt the universal validity of the theory, for they state that though sphalerite can be floated by certain amines, no insoluble sulfides or zinc salts are formed by them. Apparently the substituted hydrazines may be classed with the amines.

Thus, though there is undoubtedly much evidence of a qualitative nature in favor of this theory of adsorption, there are many cases which apparently are exceptions. Upon examination some of the exceptional cases may later be explained on the grounds of oiling, but until such exceptional cases have been classified no sweeping generalization is justified.

Many cases have been cited in the earlier paper (1) which seem to conform to the chemical theory. Firstly, concerning the mode of action of activators, e.g., copper sulfate for sphalerite, the information available suggests that this follows the order of solubility of the sulfides. The chemical theory, if applicable here, would state that lead nitrate is effective in activating sphalerite because lead sulfide is less soluble in the solution than zinc sulfide and so on, but experimental proof of this principle, which alone could decide whether the action were purely chemical, has not been advanced. Secondly, concerning the mode of action of the xanthate, it has generally been found that contact with air becomes possible at about the concentrations of metal and xanthate ions at which a precipitate of the metal xanthate forms. This is illustrated by the use of zinc sulfate to activate sphalerite. This type of evidence, which could be added to from the works of other writers, constitutes the case for the theory. Let us consider the case against it. Firstly, objections based on experimental evidence will be considered; secondly, certain theoretical objects will be discussed.

1. Some work on calcium heptoate has been cited by Gaudin and Hansen (6), which at first sight seems to support the theory. They deduce, "When the solution is saturated (with calcium heptoate) the superficial film of calcium soap (heptoate) is complete. At a concentration less than saturated, the superficial film is incomplete." A truly chemical theory implies *no* adsorption until the solution is saturated, and therefore the data may be used as an argument against the theory.

(2) It has not been shown decisively that contract first occurs under *exactly* the same conditions as precipitation. It would be difficult to prove this with the xanthates, because of their low solubility, but Gaudin's case of flotation of calcite by heptoic acid appears to be suitable for the test. Unfortunately, as pointed out above, this case does not indicate exact coincidence of these two conditions. Taggart and his collaborators have evidently noticed some similar flaws in the theory.

(3) Some unpublished work dealing with the effect of cyanide and alkali on adsorption of xanthates has shown that in many cases adsorption occurs under conditions where no heavy metal xanthate precipitation has occurred and that in others, despite the precipitation of xanthates, no adsorption of xanthate has occurred.

On theoretical grounds two difficulties arise. Firstly, it follows from the constancy of the angle for ethyl xanthate for different minerals (1), that the number of alkyl groups in the surface is independent of the mineral. The size of this group, rather than any dimensions of the crystal lattice, evidently determines the extent of adsorption. Therefore, every metallic and/or sulfide group of the surface may not be involved in anchoring the adsorption complex. Though (if this solubility or chemical theory is to hold) each xanthate ion takes the place of a sulfide ion in the surface, not every sulfide ion can be so replaced. The fate of those not replaced is uncertain. Do they pass into solution or is the final condition a mixed xanthate/sulfide surface with the xanthate portions shielding the sulfide? The solubility theory deals only with the possibility of and not with the extent of adsorption.

Secondly, the xanthates are stated by Weinig and Palmer (7) to be more soluble than the corresponding sulfides. The replacement of the sulfides of the surface by xanthates therefore needs further explanation. Taggart, Taylor, and Ince (8) and Taggart (9) have assumed that sulfides change on the surface to more soluble thiosulfates, sulfates, carbonates, hydroxides, etc.

The surface of galena can under certain conditions be changed to sulfate. Evidence has been adduced which shows that sulfate may be detected in solution after flotation of galena by xanthate. This evidence does not show, however, whether this sulfate is first formed at the surface and then replaced by xanthate, or whether it is formed by oxidation of sulfide ions which dissolve in the solution or which enter it as the result of metathesis with the xanthate. It would seem impossible to devise experiments to distinguish between these possibilities. It is perhaps significant that anglesite (natural lead sulfate) is more difficult to float than galena.

Accurate solubility determinations of xanthates and sulfides might prove it unnecessary, however, to assume the formation of any oxidized compounds on the surface. Even though the xanthate were more soluble than the sulfide, it is conceivable that the relatively high xanthate ion concentration might displace the equilibrium

$$PbS + 2X^- = PbX_2 + S^{--}$$

sufficiently to the right to allow the formation of lead xanthate on the surface.

The adsorption of xanthates by the noble metals (see following paper) can hardly be explained by metathesis. Excluding the doubtful possibility of surface oxidation, it must be concluded that xanthate ion or xanthic acid is directly adsorbed. Such a conclusion is at variance with the solubility or chemical theory of adsorption.

The balance of the evidence appears to be against the chemical theory, and for the present it is suggested that in its place there should be substituted the generalization, "The ability of a mineral to adsorb a soluble chemical flotation collector containing sulfur is closely related to the solubility of the salt formed by the collector and the metal of the mineral."

Concerning the second question, the time required after the mineral is placed in a xanthate solution before contact with air can be effected, was discussed very briefly in the paper previously mentioned (1). This discussion was concerned mainly with the development of the full equilibrium angle. Flotation, however, is possible, provided that an angle is possible— not necessarily the equilibrium angle— and it is therefore desirable to consider the speed with which sufficient adsorption occurs to enable any contact to occur.

Using any of the common sulfide minerals except galena, if contact is going to take place it is usually possible as soon as the bubble can be brought into contact with its surface after its immersion in the xanthate solution (25 mg. per liter). Even where activation is necessary, e.g., where sphalerite must be activated by copper sulfate, response is equally rapid. With lower xanthate concentrations adsorption may be a little slower, but generally, if contact is going to be possible, there is some indication of it within a minute or two. Other collectors (see the following paper) are adsorbed just as quickly.

Using galena, a second reaction apparently is possible which may interfere with the standard method used by us of detecting an adsorbed xanthate film. The nature of this reaction is at present unknown. It is prevented or removed by violent agitation of the test specimen with fine particles of galena or sand, such as would normally occur in a flotation machine. It is removed also by wiping the surface with a pad of linen, a process more easily carried out than agitation in a miniature flotation machine. It is now customary to wipe the surfaces of all minerals with linen prior to making the final measurements of contact angle. Generally, this is without effect on the angle, but occasionally, as in this case, or where a fine precipitate has settled on the surface, it is essential. Wiping the surface in this way does not remove the xanthate film. It is surmised that, where it is effective, the pad of linen removes an irregular film of some precipitate which has formed or settled on the surface and which mechanically prevents contact between the bubble and the adsorbed film on the surface.

With these precautions a chalcopyrite surface responds *fully* to 1 mg. per liter of potassium ethyl xanthate within five minutes and a galena surface within ten minutes.

Comparatively little attention has been paid in this laboratory to measurements of the rates of adsorption of xanthates by mineral surfaces. Arising out of earlier work the conviction has grown that an ideal flotation process must be based upon conditions where only one of the minerals to be separated is responsive to air, the other being completely non-responsive. Processes based upon differences in the rate of adsorption of xanthate have not appeared attractive.

The third question—the relationship between the angle of contact and the constitution of the collector—has been discussed in the paper already referred to (1). It is considered in greater detail in the next paper.

We wish to thank Mr. H. Hey for his constructive criticism in the preparation of this paper.

REFERENCES

(1) Wark and Cox: Am. Inst. Mining Met. Engrs., Tech. Pub. 461.

(2) Gaudin, Haynes, and Haas: Flotation Fundamentals, Part 4. University of Utah, 1930.

(3) Taggart, Taylor, and Knoll: Am. Inst. Mining Met. Engrs., Milling Methods, p. 247 (1930).

(4) PANETH AND HOROWITZ: Z. physik. Chem. **89**, 513 (1919).
(5) FAJANS AND HOROWITZ: Z. physik. Chem. **97**, 478 (1921).
(6) GAUDIN AND HANSEN: Flotation Fundamentals, Part 1. University of Utah, 1928.
(7) WEINIG AND PALMER: Quart. Colo. School Mines **24**, No. 4 (1929). The Trend of Flotation.
(8) TAGGART, TAYLOR, AND INCE: Am. Inst. Mining Met. Engrs., Milling Methods, p. 285 (1930).
(9) TAGGART: J. Phys. Chem. **36**, 130 (1932).

THE PHYSICAL CHEMISTRY OF FLOTATION. III

THE RELATIONSHIP BETWEEN CONTACT ANGLE AND THE CONSTITUTION OF THE COLLECTOR[1]

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Wark and Cox (1) demonstrated that the contact between air and mineral induced by potassium ethyl xanthate led to the development of a contact angle which was independent of the nature of the adsorbing solid and of the concentration of the xanthate; that another compound containing the ethoxy group, namely, sodium diethyl dithiophosphate, led to the same angle; that in the homologous series each xanthate led to a different angle, the size of the angle increasing with the number of carbon atoms in the alkyl group; and that several compounds containing substituted phenyl groups led to a substantially common angle. It was concluded that unimolecular films of these compounds were adsorbed at the surface of the adsorbing solid; that the collector molecules were orientated in such a way that the alkyl or aryl group was outermost and that they were packed as closely as the superficial area of the molecule would permit. It was also suspected that the non-polar group would prove to be entirely responsible for the magnitude of the angle of contact. The data of the present paper support these conclusions. They are also consistent with the theory that there is a close connection—not necessarily an identity—between adsorption of a collector and insolubility of its heavy metal salts.

It is to be emphasized that only sulfur-bearing compounds have been tested, and until other types of compounds have been investigated there must remain some uncertainty whether the angle of contact is completely independent of the polar group of the collector, to which, however, must be attributed its adsorption. Table 1 summarizes the results obtained to date. The blanks indicate that no measurements were made.

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[1] This work was done during the tenure of a Bartlett Research Scholarship at the Melbourne University, held by one of the authors (E. E. W.). It arose from observations made in the Flotation Research Laboratory of the University of Melbourne. This laboratory is maintained by a group of six mining companies, namely, the Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Company of Australasia Ltd., Mount Lyell Mining & Railway Company, and Burma Corporation Ltd., and the other author (I. W. W.) is directly employed by these companies.

TABLE 1

Dependence of angle of contact on nature of adsorbed compound

(Abridged summary*)

ORGANIC TYPE	SPECIFIC NON-POLAR GROUP					
	Methyl	Ethyl	Butyl	Benzyl	Phenyl	Other cyclic derivatives
Disubstituted dithiocarbamate	50	60	—	—	—	68
Mercaptan	—	60	74	71	70	69 to 71
Xanthate†	50	60	74	72	—	71 to 75
Dithiophosphate	—	59	—	—	—	—
Trithiocarbonate	—	61	74	—	—	—
Monothiocarbonate	—	61	73	—	—	—

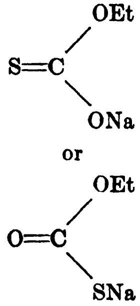
* This summary does not include the results for several non-polar groups which were investigated in one compound only These follow in later tables.

† The results for the xanthates and for diethyl dithiophosphate are taken from the paper by Wark and Cox (1).

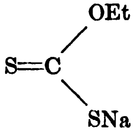
The following ethyl derivatives having thus given identical angles, it may be concluded that the number of ethyl groups in the compound influences neither the angle of contact nor the packing of the surface groups.

H—S—Et

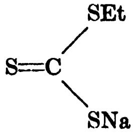
Mercaptan



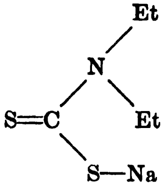
Monothiocarbonate



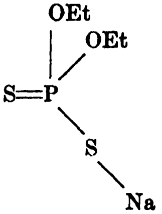
Dithiocarbonate



Trithiocarbonate



Dithiocarbamate



Dithiophosphate

It is of interest to compare the angle of contact at a unimolecular film with that at the surface of a solid containing the same surface group.

Unimolecular film of thiophenol	70°
Solid diphenyl surface ..	81 to 87°
Solid diphenyl ether surface	approximately 90°

The unimolecular film is evidently more polar than the solid compound.

EXPERIMENTAL METHOD

The method of measurement of contact angle has been described in detail by Wark and Cox (1). It is based on the method of Taggart, Taylor, and Ince (2), the important innovation being in the preparation of the mineral specimen by polishing. Polishing gives a reproducible surface at which the hysteresis is a minimum. A test of cleanliness is available, viz., that an air bubble will not make contact with a "clean" surface of any of the common sulfide minerals, of the metals, or of the common gangue minerals.

Briefly, the method of experiment is as follows: An air–mineral–water contact is effected at a horizontal surface by bringing a small bubble of air downwards into contact with the surface of a submerged mineral or metal specimen. A magnified image of the contact is projected on to a ground glass plate on which the angle of contact is easily measured. It is necessary to tap the support lightly to overcome the hysteresis effect. Recorded angles are the mean of at least six measurements. Duplicates agreed within 2°.

EXPERIMENTAL RESULTS

A. Adsorption of dithiocarbamates

The ammonium salts of the dithiocarbamates crystallize at room temperature from a mixture of the corresponding amine, carbon bisulfide, and ammonia. After extraction with acetone the product is sufficiently pure for testing; attempts at recrystallization generally lead to decomposition.

Table 2 presents the results for the compounds of this type. In many cases a mineral fails to respond to the compound unless "activated" by a heavy metal salt. Wark and Cox showed that sometimes the addition of a salt of the metal whose sulfide is being tested is sufficient to effect activation, but more often it is necessary to add the salt of a metal forming a less soluble sulfide. In the table, cases where activation is necessary are marked (a) or (b) respectively, corresponding to those two modes of activation. The symbol (p) signifies that the angle of contact was determined in a solution containing pyrogallol, which inhibits the formation of interfering oxidation products in the manner described later.

No attempt was made to determine the minimum effective concentration of any of the reagents employed; the aim was to determine the equilibrium contact angle under such conditions that contact was possible.

When using the diethyl dithiocarbamate, 25 mg. per liter of the salt generally sufficed. There was difficulty, however, in effecting contact at a pyrite surface, owing to very rapid fouling by the iron salt; this is formed because of the rapid rate of solution of the mineral.

Corresponding to the relatively high solubility of the heavy metal salts of dimethyl dithiocarbamic acid, high concentrations of the ammonium salt were necessary to induce adsorption. A 1 g. per liter solution was used throughout. Even with this concentration and using 10 mg. per liter of the specified activating agent, the full angle of contact developed only slowly for pyrite, galena, and sphalerite, but some contact occurred within an hour. Chalcopyrite responded fully within an hour. Failure to obtain a satisfactory angle for bornite was due to the surface becoming fouled by a precipitate of the copper salt.

TABLE 2

Contact angles at mineral surfaces in the presence of dithiocarbamate

MINERAL	DITHIOCARBAMATE					PIPERIDINIUM PIPERIDYL DITHIOFORMATE	DIMETHYL-DIPHENYL-THIURAM DISULFIDE
	Dimethyl	Diethyl	Monophenyl	Phenylmethyl	Phenylethyl		
Galena	50 (a)	59	54	50	61	70 (a)	50
Sphalerite	50 (b)	59 (b) 59 (b)	55 (b) 52 (b)	50 (b)	61 (b) 60 (a)	67	50 (b)
Pyrite ...	50	58	54 (p)	50	61	70	50
Chalcopyrite	50	59	—	49 (p)	62	67	50
Bornite.	Irregular	62	54	50 (p)	62	67	50
Average	50	60	54	50	61	68	50

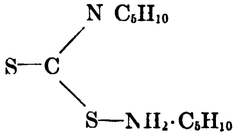
A higher concentration (a 1 g. per liter solution was used throughout) was also necessary with the methylphenyl compound, but the reaction was more rapid than with the dimethyl compound, 30 minutes usually sufficing for the maximum angle to be reached. Sphalerite, activated by 10 mg. per liter of silver sulfate, gave the customary methyl angle of 50°, but sphalerite, activated by 10 mg. per liter of cupric sulfate hydrate, and also the copper minerals gave a higher contact angle, 65°. This was attributed to the formation of a compound analogous to dixanthogen. Wark and Cox (1) have shown that dixanthogen, when present in the form of an emulsion which "oiled" the surface, gives a higher angle than xanthate. Dixanthogen tends to form spontaneously in xanthate solutions of this strength and it is probable that its analogue forms in dithiocarbamate solutions.

In further tests on the copper minerals, oxidation was prevented by the addition of pyrogallol (5 g. per liter). The normal angle was then obtained.

Twenty-five hundredths of a gram per liter of sodium sulfite was equally effective. Independent tests demonstrated that pyrogallol and sodium sulfite were without influence on the contact angle in normal cases and that they prevented the formation of dixanthogen under conditions where it would normally be slowly formed.

The corresponding dithiocarbamate oxidation product, namely, dimethyldiphenylthiuram disulfide was prepared. The response to this compound is rapid and a concentration as low as 15 mg. per liter is effective. Being a solid, it cannot oil the surface. It is not surprising, therefore, that it led to the same angle as the simple dithiocarbamate, but this leaves us at a loss to account for the high angle shown by the copper minerals in the absence of reducing agents.

Piperidinium piperidyl dithioformate,



is a member of the dithiocarbamate series. It has a closed ring in place of two alkyl groups

The piperidinium salt is obtained more easily than the ammonium, but both would ionize and their absorption reactions would be identical. It is surprising that the angle corresponding to this compound, 67 to 70°, is not closer to that for cyclohexanyl xanthate, 75°, but this indicates that the *whole* of the outermost group must be considered in predicting the contact angle. As the surfaces of the minerals were fouled very rapidly by precipitation of the heavy metal dithioformate, the maximum angle of contact was obtained only after wiping them free from precipitate with a small pad of linen.[2]

No abnormalities were observed with the phenylethyl compound except a tendency for bornite to give an angle slightly above normal, viz. 66°. This was not apparent in the presence of pyrogallol.

The results for the phenylethyl and diethyl compounds are identical. This may mean that in the former only ethyl groups are in the surface. Likewise the methylphenyl and dimethyl compounds yield identical angles.

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[2] Angles are checked in this manner as a matter of routine; usually the wiping leaves the angle unaffected, but occasionally, as in this case, it is essential. Wiping in this manner corresponds to the agitation of the pulp in a flotation machine.

Though the angle for the phenyl group is 70°, monophenyl dithiocarbamate gives only 54°. It must be concluded therefore that both the hydrogen atom and the phenyl group influence the contact angle.[3]

Unsubstituted dithiocarbamate.—Ammonium dithoicarbamate, tried in various concentrations and with various activators, gives no reaction with pyrite or chalcopyrite. The concentrations employed were sufficient to give precipitates of iron and copper dithiocarbamate and if, as seems reasonable, it be concluded that the compound was absorbed, the unsubstituted amino group must give a zero angle of contact, i.e., it must be too polar for air attachment.

TABLE 3

Contact angles at mineral surfaces in the presence of mercaptans

MINERAL	ETHYL MERCAPTAN 500 mg per liter	*n*-BUTYL MERCAPTAN	BENZYL MERCAPTAN	THIOPHENOL	THIOCRESOL	THIO-β-NAPHTHOL
Galena	0	73	71	68	71 68 (p)	70
Sphalerite	62 (b)	74	70 (b) 72	71 (b)	70 (b)	70
Pyrrhotite	—	—	—	71	—	—
Pyrite	57	74 (p)	69 (p)	71	72	68
Chalcopyrite .	62	74 (p)	72 (p)	71	70	70
Bornite	—	—	72 (p)	—	71 (p)	—
Chalcocite	—	—	—	—	71 71 (p)	—
Covellite.	—	—	—	—	72	—
Average.	60	74	71	70	71	69

B. Adsorption of mercaptans

The compounds used were the purest available commmercially. It is known, however, that the mercaptans tend to oxidize spontaneously, the corresponding disulfides being formed. Oxidation would be helped by the presence of cupric and/or ferric ions. Consequently it was anticipated that, in testing the mercaptans, trouble would be experienced of a kind similar to that previously encountered with some xanthates. Such was indeed the case, abnormally high angles having been obtained in the following cases: thiocresol with bornite, benzyl mercaptan with all the copper and iron minerals, butyl mercaptan with pyrite and chalcopyrite (see table 3). The addition of pyrogallol (in these cases 5 g. per liter was used) was again effective in overcoming this difficulty.

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[3] This same angle has been obtained at the surface of certain copper minerals in the presence of thiocarbanilide. Both compounds contain the $-\mathrm{N}\langle^{\mathrm{Ph}}_{\mathrm{H}}$ group.

Ethyl mercaptan and its heavy metal salts are relatively soluble in water. The customary 25 mg. per liter solution is not effective, but a 500 mg. per liter solution proved satisfactory for chalcopyrite, pyrite, and for sphalerite activated by 10 mg. per liter of silver sulfate. No contact was obtained with galena using 500 mg. per liter of the reagent, even in the presence of 25 mg. per liter of lead acetate. Activators of type (b) would probably have been effective. Higher concentrations than 25 mg. per liter of *n*-butyl mercaptan were also necessary; 500 mg. per liter sufficed for chalcopyrite and pyrite and 1 g. per liter for galena and sphalerite. A saturated solution of cetyl mercaptan failed to cause contact between the mineral surfaces and air. This may have been due to the very low solubility of the compound. Saturated solutions of thiocresol and thio-β-naphthol were used; these contain less than 25 mg. per liter. With benzyl mercaptan and thiophenol 25 mg. per liter solutions were employed.

TABLE 4

Contact angles at mineral surfaces in the presence of xanthates

MINERAL	*n*-OCTYL XANTHATE	SECONDARY OCTYL (CAPRYL) XANTHATE
Galena	85	90
Sphalerite	87 (b)	90 (b)
Pyrrhotite	85	90
Pyrite	86	90
Bornite	85	92
Average	86°	90°

C. Adsorption of xanthates

The adsorption of a number of xanthates was described by Wark and Cox (1). Only two additional xanthates have been prepared and tested, viz., *n*-octyl and *secondary* octyl. The results for these two compounds are in table 4. Sphalerite responds without activation but the full angle of contact is attained very slowly.

D. Adsorption of diethyl dithiophosphoric acid

Table 5 shows the results for the sodium diethyl dithiophosphate, which was obtained by courtesy of the American Cyanamid Company, which markets it under the trade name "Sodium Aerofloat."

Sodium diethyl dithiophosphate is more soluble than the corresponding xanthate; activation is therefore necessary for a greater number of the minerals. An angle of 80° sometimes develops; this is probably due to an oxidation product.

E. Adsorption of trithiocarbonates

The potassium salts of the trithiocarbonates crystallize from ice-cooled mixtures of potassium hydroxide, carbon bisulfide, and the corresponding mercaptans. They were recrystallized from a mixture of ether and benzene. Table 6 gives the results for the compounds of this type. Twenty-five milligrams per liter of trithiocarbonate was used throughout.

TABLE 5

Contact angles at mineral surfaces in the presence of sodium diethyl dithiophosphate

MINERAL	SODIUM DIETHYL DITHIOPHOSPHATE
Galena	58 (b)
Sphalerite	59 (b)
Pyrrhotite	59 (b)
Pyrite	59 (b)
Chalcopyrite	60
Chalcocite	60
Average	59

TABLE 6

Contact angles at mineral surfaces in the presence of trithiocarbonates

MINERAL	TRITHIOCARBONATE	
	Ethyl	Butyl
Galena	61	73
Sphalerite	60 (p) (b)	73
Bornite	60 (p)	74 (p)
Chalcopyrite	61 (p)	74 (p)
Pyrite	61 (p)	74 (p)
Average	61	74

F. Adsorption of monothiocarbonates

The potassium monothiocarbonates were prepared by passing carbonyl sulfide, generated from sodium thiocyanate and a 50 per cent aqueous solution of sulfuric acid, into a solution of potassium hydroxide in the corresponding alcohol. They were recrystallized from alcohol and washed with ether. Table 7 gives the results for these compounds.

The heavy metal salts of ethyl monothiocarbonic acid are relatively soluble. Chalcopyrite gives the full angle at a concentration of 25 mg. per liter, but with activated sphalerite 300 mg. per liter was necessary. Galena and pyrite gave no reaction with either 25 mg. per liter or 500 mg. per liter, but would no doubt respond to activators of type (b). The butyl monothiocarbonates are also too soluble for immediate or complete response to 25 mg. per liter of the potassium salt except in the case of bornite. The full angle, however, develops slowly without activators for all the minerals except sphalerite, and more rapidly with higher concentrations of the collector or with activators present. Galena evidently requires an activator to give the equilibrium value as the angle was somewhat low after five hours.

TABLE 7

Contact angles at mineral surfaces in the presence of monothiocarbonates

MINERAL	MONOTHIOCARBONATE	
	Ethyl	Butyl
Galena	0	(69)
Pyrite	0	72
Chalcopyrite	61	74
Sphalerite	61 (b)	72 (b)
Bornite	—	74
Average.	61	73

TABLE 8

Angle of contact at metal surfaces in the presence of ethyl xanthate

METAL	ANGLE OF CONTACT	NOTES
Gold	61	
Silver .	60 (p)	
Platinum	58	
Copper	60 (p)	
Tin . . .	61	Polished on lead
Bismuth	61	
Antimony	58	
Arsenic	60	
Selenium	60	
Cadmium	60	Polished on lead
Zinc	Nil	Does not respond to activation by copper or silver salts
Iron	Nil	The surface fouls with extreme rapidity
Lead.	Irregular	Surface produced by cutting; the surface became fouled too rapidly for satisfactory measurement
Average	60°	

The solubility of the heavy metal salts of the thiosubstituted carbonates is, in order of decreasing solubility:—monothiocarbonates, dithiocarbonates, trithiocarbonates. The readiness with which they are adsorbed by minerals increases in this order.

G. Adsorption of ethyl xanthate at metal surfaces

The metal surfaces were prepared and tested in the same manner as the sulfide minerals. A 52 mg. per liter solution of potassium xanthate was used. Table 8 gives the results for the metals tested. The failure of zinc and iron to respond may be due to too great reactivity of the surface with water.

SUMMARY

The angles of contact due to several different types of flotation "collectors" have been investigated. The types investigated were xanthate, mercaptan, dithiocarbamate, dithiophosphate, trithiocarbonate, and monothiocarbonate.

It has been demonstrated that, when contact occurs, the angle at the line of triple contact air–solid–solution is dependent only upon the nonpolar group of the adsorbed "collector." It is independent of the nature of the solid, of the polar or anchoring group of the collector, and of the concentration of the collector.

Whether adsorption of the collector occurs at a mineral or metal surface is related to the solubility of the corresponding metal salt of the collector.

We wish to record our thanks to Professor E. J. Hartung for having made available a laboratory for carrying out our research, and to Messrs. H. Hey and A. B. Cox for their help and criticism.

REFERENCES

(1) Wark and Cox: Am. Inst. Min. Met. Engrs., Tech. Pub. No. 461 (1932).

(2) Taggart, Taylor, and Ince: Am. Inst. Min. Met. Engrs., Milling Methods, p. 285 (1930).

THE PHYSICAL CHEMISTRY OF FLOTATION. IV

A Criticism of Ostwald's Theory of Flotation

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Wo. Ostwald (1) has advanced a theory of the action of soluble collectors, an essential part of which is that only a ring of the collector is necessary for flotation, the location of the ring being the air–water–mineral line of contact. The process by which this ring is assumed to be held is styled by him "adlineation." This theory is in opposition to that adopted by us (2), namely, that for soluble collectors a substantially complete unimolecular film is adsorbed by the surface of the mineral, and that for oleaginous collectors a continuous thin film spreads over the surface. The only evidence advanced by Ostwald in direct opposition to this view is a statement based on an observation of Kellermann (3) that the amount of added reagents is insufficient to form such a unimolecular film. This evidence has been questioned by Siedler, Moeller, and Reddehase (4), who cite work by Gaudin, Glover, Hansen, and Orr (5) which demonstrates that the amount of collectors used in practice is of the order required to form a unimolecular film over the surface of the mineral floated. Ostwald, in reply, questions the assumptions upon which Gaudin's and Siedler's calculations are based, but does not offer any further substantiation for Kellermann's views, and, in fact, admits the impossibility of determining accurately the number of molecules adsorbed per unit area of the mineral surface, except by a complete adsorption analysis.

In our opinion, it has not been proved that in any single case the number of effective collector molecules (certain frothers are also collectors) is insufficient to form a unimolecular film, but, apart from this, there is so much evidence against Ostwald's "adlineation" theory that even if, as seems unlikely, it were proved that Kellermann's view is correct, some explanation other than Ostwald's must be sought. Though finality has not been reached in deciding between the views of Kellermann and Gaudin, it is certain that in practice quantities of reagents must be added enormously in excess of those required to give an "adlineation" ring, and as it is impossible with the available technique to determine what fraction of these reagents is consumed by the minerals floated, any direct proof or disproof along these lines is impossible.

Indirect methods must therefore be adopted in determining whether the theory possesses the essential desiderata of a useful working theory. A theory need not be true to be useful, but to be useful a new theory should be simpler and more comprehensive than previous theories, and it should be in accord with known facts. Being an extreme development of the unimolecular film theory, Ostwald's theory cannot claim greater simplicity than it, and, not being applicable for insoluble collectors, it is not as comprehensive as the theory of complete filming. More important, the "adlineation" theory is not in accord with several experimental facts and accredited principles of surface physics.

Considering the turbulent conditions of the flotation pulp it is doubtful whether a ring of collector of the type suggested by Ostwald could lead to a sufficiently stable contact between air and mineral. Only if the ring acted as a perfectly mobile barrier could the air–mineral aggregates withstand the sudden stresses imposed upon them. Ostwald, in his second paper, attempts to show how the "adlineation" ring possesses this necessary mobility. Great mobility, however, could arise only from one of two causes. Firstly, the line of collector might be so loosely bound to the surface that free motion could occur. Actually xanthate films, far from being loosely held, are held by the surface with great tenacity. For example, chalcopyrite retains a xanthate coating after being washed for several minutes in running water, as is shown by the contact angle remaining the same as in a xanthate solution. Such tenacious adsorption is of considerable importance, since the xanthate film is the link which holds the mineral to the bubble. Secondly, great mobility might be due to the ring of the collector being securely bound to certain atoms of the crystal lattice which themselves possessed great mobility in the surface. Though this type of mobility is assumed for liquid films, we know of no evidence suggesting sufficient mobility of the atoms of a solid. Indeed Adam (6) states: "As a general rule, spreading on solids only occurs through the vapour . . . .; if the liquid is non-volatile, no spreading occurs, at least in any reasonable time." Adam's reference was to solids in contact with the atmosphere, but the generalization may apparently be extended to include contact with a liquid phase, in which case spreading only occurs through solution. Our experience would support such an extension, for the methods of experiment adopted in this laboratory would not have been possible had adsorbed films possessed appreciable mobility. Only one side of our test specimens of mineral is protected from contamination, and it is known that at least portions of the other sides are contaminated by grease and/or air, but experiment has shown that the area of contamination does not spread to the test face.

Perhaps the most convincing argument against great mobility is the phenomenon known as hysteresis. Several observers (7) have noticed that the air–mineral–water boundary is not perfectly mobile. The imperfect mobility is responsible for a difference between the angles of contact when water is replacing air and when air is replacing water at the mineral surface. The difference between these two angles has been called the hysteresis; it is due to friction.

The existence of a definite contact angle at the line of triple contact between air, water, and mineral has been accepted by Ostwald. It is universally accepted that if T_{as}, T_{wa}, and T_{sw} signify the surface energies at the air–solid, water–air, and solid–water interfaces, respectively, the magnitude of the angle of contact θ is determined by the relationship,

$$\cos \theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

DeWitt, Roper, and Makens (8) have shown that the magnitude of T_{wa} is practically unaltered by common collectors and frothers at the concentrations customarily employed. If, as Ostwald suggests, there is but a ring of collector at the line of triple contact, the air–solid and solid–water interfaces on either side of this line cannot be influenced by the collector, and the magnitudes of their interfacial energies would be identical with the corresponding values in pure water. Thus, if the "adlineation" theory were correct, the angle of contact would be independent both of the addition of a collector and of its nature. This is contrary to experience. At clean surfaces of many of the common minerals the angle of contact in pure water is zero, and if a collector be added the resultant finite angle varies with the nature of the essential non-polar radical of the collector (2).

Ostwald repeatedly stresses a generalization of Mayer that only unwettable particles float. We will return to a more exact statement of this principle later, but far from agreeing better, as Ostwald suggests, with his own theory than with other theories, Mayer's generalization is quite incompatible with Ostwald's theory, for it is only after the surfaces of the sulfide minerals have been changed by the collector that they become "unwettable." Furthermore, experiment shows that the whole of a collector-conditioned mineral surface is actually different from a surface which has had no contact with collector; the change is not confined to a single line on the surface or to any small fraction of the surface. For if the specimen be washed and placed in distilled water a bubble of air will effect contact with any part of the surface even though the surface be "swept" several times by air bubbles.

It is well to consider what is meant by the term "unwettable." Ostwald cites Edser (7) as stating that in no known case does the angle of contact at the air–water–solid boundary reach 180°. This implies that when contact with air is possible, equilibrium can be established with a portion of the solid surface in contact with air and a portion with water, the air–water interface being inclined at an angle to the solid suface. The extent of the displacement of the water from the surface depends upon the volume of the air, the angle of contact, and the size and shape of the surface of the particle. The term "unwettable" is, therefore, misleading, and we suggest in place of Mayer's generalization the statement, "No particle will float at an air–water interface unless both air and water are in contact with its surface, that is, unless there is a finite contact angle at a line of triple contact between air, solid, and water."

At surfaces of substances such as diphenyl and paraffin wax, water is readily displaced by air, the equilibrium contact angles being approximately 84° and 105°, respectively, for the above two substances. Bubbles of air will readily attach themselves to such solids, and particles of diphenyl (sp. gr. = 1.16) may be floated readily to the surface of water. There is, moreover, no visible difference between the type of contact of an air bubble with diphenyl and with a mineral surface which has been in contact with a soluble collector, nor in the type of flotation. Since the surface of diphenyl must consist exclusively of hydrocarbon groups, there is no possibility of the presence of a mobile triphilic[1] ring at the line of triple contact. Ostwald's theory, therefore, cannot have universal application in accounting for the mechanism of flotation.

Indeed, Ostwald does not use the "adlineation" theory for oleaginous collectors. For these he makes use of a theory of "laminar" flotation. This theory was propounded in very similar terms by Christmann (9). The essential feature of the theory is that superimposed on the collector film at the mineral surface there is a second film composed of frother molecules and that the dual film is air-avid and induces flotation. Ostwald states that there must be an adherence between the collector and frother films, and Christmann that an orientated hydrocarbon film of collector is soluble in the hydrocarbon film of the frother. The orientation of the frother molecules necessary for these conditions to be fulfilled, however, would be such that the assumed dual film could not be air-avid. The collector is bound to the mineral surface by its active group, the non-polar group being orientated away from the mineral. The frother molecule, if it be soluble in this film as Christmann suggests, or if it adhere as Ostwald suggests, must therefore be orientated with its non-polar group towards, and its polar or water-avid group away from the mineral. Therefore, the dually filmed particle could not float. Actually the orientation of the frother molecule at the air–water interface is such that its non-polar group is directed towards the air phase and the polar group towards the water phase; such orientation would oppose any adherence or mutual solubility of the collector and frother films.

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[1] Ostwald considers that soluble collectors must be of a triphilic nature, i.e., contain three groups of essentially different type, whose function is to stabilize the air–water–mineral contact, each group of the collector making contact with only one phase. Since the hydrocarbon groups in the surface of diphenyl can make contact with both air and water such an hypothesis is not essential to account for flotation. Moreover, it would require abandonment of the usual conceptions of atomic attractions to ascribe a triphilic nature to such soluble collectors as the quaternary ammonium salts and mercaptides.

It is our view that the essential function of the frother is to stabilize the large air–water interface necessary for froth flotation, which stabilization is undoubtedly achieved because of adsorption (either positive or negative) at this interface. During the process of formation of the air–mineral aggregate the frother is squeezed from the surface of the bubble, and air then makes direct contact with the air-avid collector film. This collector film on the mineral surface may be an orientated adsorbed unimolecular layer, as in the case of soluble collectors, or a more discrete film of an insoluble collector as in the case of oils. The difference between soluble and insoluble collectors does not therefore lead to a difference in the mechanism of formation and stabilization of air–mineral aggregates, but to a difference in the means by which they render a mineral surface air-avid. It is thus unnecessary to postulate a number of complex theories of flotation to cover the use of different types of collectors.

REFERENCES

(1) Ostwald, Wo.: Kolloid-Z. **58**, 179 (1932); **60**, 324 (1932).
(2) Cox and Wark: J. Phys. Chem. **37**, 797 (1933).
(3) Kellermann: Kolloid-Z. **47**, 273 (1929).
(4) Siedler, Moeller, and Reddehase: Kolloid-Z. **60**, 318 (1932).
(5) Gaudin, Glover, Hansen, and Orr: Flotation Fundamentals, Part I. University of Utah, 1929.
(6) Adam: The Physics and Chemistry of Surfaces, p. 213. Clarendon Press, Oxford (1930).
(7) Sulman: Trans. Am. Inst. Mining Met. Engrs. **29**, 44 (1919–20).
Edser: Brit. Assoc. Fourth Report on Colloidal Chemistry **4**, 263 (1922).
Langmuir: Trans. Faraday Soc. **15**, 62 (1920).
Adam and Jessop: J. Chem. Soc. **127**, 1865 (1925).
Wark and Cox: Am. Inst. Mining Met. Engrs., Tech. Pub. No. 461.
(8) DeWitt, Roper, and Makens: J. Am. Chem. Soc. **54**, 444, 455 (1932).
(9) Christmann: Am. Inst. Mining Met. Engrs., discussion following Tech. Pub. No. 461.

COMMUNICATIONS TO THE EDITOR

THE THEORY OF THE STICK ANTIMONY ELECTRODE

The stick antimony electrode is a type of the metal–metal oxide electrode, the antimony oxide being present as an adsorbed film on the surface of the metal. This oxide is formed by air oxidation on the metal surface after polishing. The reaction of this adsorbed film with the hydrogen-ions in the solution sets up a potential, according to the reaction (Roberts and Fenwick: J. Am. Chem. Soc. **50**, 2125 (1928)):

$$Sb_2O_3 + 6H^+ + 6(-) = 2Sb^0 + 3H_20$$

The potential is found by the Nernst equation:

$$E = E_c - \frac{RT}{6F} \ln \frac{(Sb_2O_3)(H^+)^6}{(Sb^0)^2(H_2O)^3}$$

Developing the equation:

$$E = E_c - \frac{RT}{6F} \ln (H^+)^6 = E_c - \frac{RT}{F} \ln (H^+) = E_c + 0.05915 \text{ pH}$$

This potential is identical with that developed from the solution of the metal forming its ions in a solution saturated with the metallic oxide.

However, it is not necessary for the solution being measured to be saturated with the insoluble oxide for the metal–metal oxide electrode to function correctly. Tartar and McClain (J. Am. Chem. Soc. **53**, 3201 (1931)) have stated that the potential of a metal electrode is due "to an adsorbed ionic film extending from the electrode a measurable distance out into the solution." Since this is so, an adsorbed oxide film on a metal electrode will furnish saturation of that portion of the solution from which the potential is derived. From this it would seem that the electrode reaction takes place at the interface of the metal with its oxide.

In preliminary work with several stick metal electrodes, as antimony, bismuth, tungsten and tantalum, the potential obtained seemed to be dependent on the nature, thickness and stability of the oxide film on the metal. The oxide should be a definite compound, not a mixture of oxides, and of specific crystalline form (Roberts and Fenwick: J. Am. Chem. Soc. **50**, 2125 (1928)). The thickness of the film should be such that it will allow penetration of the solution to the metal. A thick film of the oxide on a metallic stick tends to slip off, as a glove from the finger. This supports the contention that the electrode reaction takes place at the interface of a metal with its oxide. If the oxide film dissolves, ions will be formed in the solution which will affect the potential being measured. It would seem that any stable metal which could have an adsorbed film of its compound insoluble in the solution might function as a measure of the hydrogen-ion concentration of that solution.

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THE THEORETICAL LIMITATIONS OF THE STICK ANTIMONY ELECTRODE

In a recent paper (Parks and Beard: J. Am. Chem. Soc. **54**, 856 (1932)) the authors have shown that stick antimony electrodes in unstirred buffer solutions in contact with air may be calibrated to give a curve which agrees with that of the hydrogen electrode as to slope, thus satisfying the Nernst equation from the pH value of 1.60 to that of 7.87.

In a highly acid solution, pH lower than 1.60, the potentials obtained with the stick antimony electrode are not a true measure of the pH of the solution, because the adsorbed film of Sb_2O_3 on the metal electrode has dissolved and antimonyl ions have been formed according to the reaction

$$Sb_2O_3 + 2H^+ = 2SbO^+ + H_2O$$

Antimonyl ions with hydrogen-ions in equilibrium with the antimony metal and water develop a potential (Schuhmann: J. Am. Chem. Soc. **46**, 52 (1924)) which may be found by the Nernst equation:

$$E = E_0 - \frac{RT}{3F}\ln\frac{(SbO^+)(H^+)^2}{(Sb^0)(H_2O)} = E_0 - \frac{RT}{3F}\ln\,(SbO^+)(H^+)^2$$

Thus the concentration of the antimonyl ion is a factor in the potential developed and the electrode does not correctly measure the hydrogen-ion concentration of highly acid solutions.

In alkaline solutions, above pH 10.53, there is also a deviation of the values obtained by the stick antimony electrode away from the theoretical values. The deviation in this range is due to the antimonite ions (SbO_2^-) in the solution formed by the dissolving of the adsorbed film of antimony oxide on the metal stick by hydroxyl ions according to the reaction

$$Sb_2O_3 + 2OH^- = 2SbO_2^- + H_2O$$

These antimonite ions with water in equilibrium with the metal and hydroxyl ions give a potential (Grube and Schweigardt: Z. Elektrochem. **29**, 257 (1923)) which may be found by the Nernst equation:

$$E = E_0' - \frac{RT}{3F}\ln\frac{(SbO_2^-)(H_2O)^2}{(Sb^0)(OH^-)^4} = E_0 - \frac{RT}{3F}\ln\,(SbO_2^-)(H^+)^4$$

Thus in extreme alkaline solutions the potential will be that denoted by the Nernst equation involving the SbO_2^- ion, and does not give a value that is a measure of the hydrogen-ion concentration of the solution.

The deviation of the stick antimony electrode values between pH 7.87 and 10.53 away from the theoretical values is due to a differential effect of the Sb_2O_3 and the SbO_2^- ions. If the Sb_2O_3 alone were present with increasing pH (from 7.87) the curve would continue in a straight line from its lower values and give higher potentials. If, on the other hand, the SbO_2^- ion were the only antimony ion present with decreasing pH (from 10.53) lower potentials would be obtained according to the Nernst equation which has (SbO_2^-) as a factor. Grube and Schweigardt (Z. Elektrochem. **29**, 257 (1923)) state that the SbO^-_2 ion readily absorbs oxygen from the air. This excess oxygen in the solution in contact with the metal would aid in the formation of Sb_2O_3 and so retard the deviation of the values in this range.

Thus in extreme acid and alkaline solutions where there is a limited amount of antimony oxide, as in the case of an adsorbed film on a metallic stick, the potential obtained by the stick antimony electrode is not a true measure of the hydrogen-ion concentration of the solution due to the formation of oxy-antimony ions in the solution. Although the stick antimony electrode is very convenient as a means of measuring the hydrogen-ion concentration of a solution, it is theoretically correct only in the pH range from 1.60 to 7.87. In alkaline and highly acid solutions the electrode can be used only if it has been previously calibrated.

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THE RÔLE OF SURFACE ELECTRONS IN ADSORPTION AND CATALYSIS

A theory that the adsorption of gases by metals and the catalysis of reactions following this adsorption is due to some electrical or mechanical effect of the surface electrons of the metal was advanced by Pisarzhevskii (Ukrain. Khem. Zhur. 1, 1–18 (1925)) in 1925. More recently this idea has been taken up again by Nyrop (Chemistry & Industry **50**, 752–5 (1931) and Phys. Rev. **39**, 967–76 (1932)), who gives it a more theoretical and mathematical treatment. A quotation from the abstract (C. A. **22**, 2512 (1928)) of the Pisarzhevskii paper will serve to give the nature of his theory: "Catalytic activity of metals is due to freely moving electrons. Adsorption of gases by metals is the result of electrostatic forces between gaseous mols. and a film of free electrons on the surface of metals. Impacts of these electrons on the adsorbed mols. produce their dissociation and ionization and cause thereby chem. reactions."

According to Nyrop, ionization of the gas molecules precedes adsorption and will occur in cases where the metal has free electrons of sufficient kinetic energy. Once adsorption has occurred, the possibility of reaction and the course of the reaction with some other gas that may be adsorbed depends on the energy required for ionization of the resulting substance and its rate of diffusion away from the metallic surface.

In connection with a general study of the mechanism of heterogeneous catalysis started some time ago in this laboratory, experiments to test this theory were performed. A nickel strip catalyst was used in the reaction of hydrogen and oxygen. Numerous runs were made with this catalyst supposedly activated by the impression on it of a high frequency electrical current. The following may be given as argument that during such a treatment the activity of the catalyst should be increased if the Pisarzhevskii-Nyrop theory is valid.

Increase in catalytic activity should result from (1) an increase in kinetic energy of the free surface electrons, and/or from (2) an increase in their concentration. With alternating currents of 5000 cycles, a "skin effect" is generally quite appreciable (Kennelly, Laws, and Pierce: J. Am. Inst. Elect. Engrs. **34**, 1953 (1915)) and with greater rapidity of alternation this effect becomes more pronounced. With the current and its attendant heat generation concentrated on the surface of the conductor, the kinetic energy of the electrons there becomes greater than is normal for the temperature of the metallic mass as a whole.

As to concentration of the free electrons (i.e., those electrons in a metallic conductor to which classical theory ascribes conductance) on the surface, it is only necessary to consider the probable change as the frequency of an alternating current of any given strength is made greater. As the current becomes more and more a phenomenon of the surface only, either the number of free electrons on the surface must increase or their mean free path must change in order to accommodate the higher current density. Either or both of the changes should make for more collisions with gas molecules and hence greater catalytic power.

Frequencies of about 50 kilocycles with currents up to 50 milliamperes were used in the experiments. In no case was there any evidence of increased catalytic activity.

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NEW BOOKS

Thermochemie. By DR. W. A. ROTH. 102 pp.; 15 figs. Sammlung Göschen. Berlin: Walter de Gruyter and Co., 1932. Price: RM. 1.62.

This small volume by a skilled experimenter in the field contains an excellent, condensed treatment of thermochemical practice. Students who desire to become acquainted with the best methods of attacking thermochemical problems will find this book of considerable value Even the experienced thermochemist will find many useful hints scattered through this volume. The author has included a short treatment of thermodynamics. Thermochemical data appear only as illustrative material.

F H. MACDOUGALL.

Dizinario di Chimica Generale e Industriale. Volume I, A–E. By PROF. MICHELE GUIA AND DR. CLARA GIUA-LOLLINI 29 x 20 cm.; ii + 1082 pp. Turin: Urime Tipografico-Editrice Torinese (Utet), 1933. Price: L. 165.

This is a formidable first volume of a Dictionary of Chemistry, concerned not only with the theoretical aspects of the science, but also with its varied application to agriculture, biology, pharmacy, geology, and mineralogy. The whole, when completed, will be no small achievement for only two authors. In view of the existence of other seemingly similar compilations, e.g., Thorpe or Ullmann, each the combined work of many specialists, the question may be asked, what is there to justify this new work, apart from its being Italian and up to date?

The answer is that it covers new ground. The information given under each heading is, in the main, comprehensive, without very great detail, and is in general stated so simply that anyone without special knowledge of chemistry can get valuable information from it. At the same time useful references are appended for anyone who requires more. The inclusion of short biographies of past chemists, from the earliest times, and technologists of later date, and the large part of the work devoted to chemical theory and pure science, differentiate it from the dictionaries or encyclopedias dealing only with applied or technical chemistry. Indeed another Italian compilation is probably the only one on similar lines, i.e., *Nuova Enciclopedia di Chimica,* founded by Guareschi and continued by others in thirteen volumes.

In the volume under review much is open to criticism, chiefly on the ground that subjects are inadequately dealt with. More modern work is often omitted, e.g., molecular association is chiefly devoted to the work of Ramsay and Shields, or under such headings as catalysis, etc. On the other hand, many good accounts are given, e.g., of the history of the atomic theory, crystal form, chemical affinity, etc.

On the technical side the detail given is not always distributed proportionately to the importance of the subject considered, but, as is to be expected, materials important to, or products of, Italian industry are exceptionally well done, e.g , boric acid.

This first volume contains twenty-eight tables and five hundred and sixty-five illustrations. Should the succeeding volumes maintain the high standard already achieved, the whole should prove a useful and necessary work of reference.

W. H. PATTERSON.

L'Azéotropisme. La tension de vapeur des mélanges de liquides Bibliographie. By MAURICE LECAT. 24.5 x 16 cm ; viii + 264 pp. (Printed on one side of the paper only). Brussels: Lamertin, 1932. Price: 15 belgas.

Azeotropy is a subject of increasing importance both in the research laboratory and in industry, and the determinations of the vapor pressures of mixed liquids have important theoretical implications at the moment Professor Lecat has made an exhaustive study of the literature of azeotropism, and has himself examined over two thousand mixtures and discovered a great many azeotropic mixtures. Before the appearance of this volume the literature and details regarding the phenomena were collected by him in a volume published in 1918 having almost the same title as the book under review. The data in Professor Sidney Young's well-known book *Distillation Principles and Processes* (1922) and also in the *International Critical Tables*, Vol. III, p. 318 (1928), were based largely on this former volume, and we are referred to it in the Tables for further details and literature regarding the azeotropic systems there cited, each system being given a number termed Lecat's number.

The volume under review contains a list, in alphabetical order, of the authors of papers and other publications on azeotropism and the vapor pressures of liquid mixtures. The complete reference with the full title of the paper or book is given. A second more concise list arranges the works chronologically, and gives an abbreviated reference. A third list gives the journals and books, already quoted in the previous lists, in alphabetical order. Cross references are given in both of these to the first list. All the lists are printed on one side of the paper only. As is only to be expected in a work of this kind, there are a few omissions in the later years.

In the preface we are promised shortly another book entitled *Tables d'azéotropes binaires*, and it is probable that these tables will contain the azeotropic mixtures arranged by subject, and will therefore be a necessary companion volume to this one. Professor Lecat should have our thanks for having carried through an enormous task most successfully. It will be a welcome addition to the shelves of all chemical libraries.

D. C. JONES.

Third and Final Report of the Adhesives Research Committee. By the Adhesives Research Committee appointed by the Department of Scientific and Industrial Research. 24 x 15 cm.; v + 109 pp. London: H.M. Stationery Office, 1932. Price: 2/6.

The third and final report of the Adhesives Research Committee contains the report proper, together with three appendices. Appendix I describes the final stages of the work conducted by Mr. Douglas and Miss Pettifor at the Royal Aircraft Establishment on the mechanical testing of timber-glue joints. Appendix II reports further progress in the work conducted by the late Professor Schryver and his collaborators at the Imperial College of Science and Technology on the chemistry of gelatin. Appendix III describes further investigations into the nature of adhesion by Professor McBain, with Dr. Lee, at Bristol University, and later at Stanford University.

Most of the work described in the appendices has appeared already in various publications. The later stages of the research dealt with in Appendix I are given more fully here, and the conclusions of the authors as to the best type of test-piece, the most suitable timber, and the procedure best adapted for reducing in number the many experiments necessary to arrive at a representative value for a certain glue, are given with complete tabulated experimental results, and numerous illustrations.

Appendices II and III both contain discussions of work of great interest to chemists. Professor Schryver (with Dr H W. Buston) describes in a general way his work on the purification of gelatin, and gives a more detailed account, in chronological order, of the work done on the intramolecular changes that gelatin undergoes. A short section is devoted to the methods of protein analysis, but this part of the work remains incomplete Appendix III is divided into six parts, the heads to which give a rough idea of the comprehensiveness of the treatment by Professor McBain. Part I is a general survey of the new results; Part II contains the work on pure chemical substances as adhesives; Part III deals with the adhesion of gums, resins, and waxes to metals; Part IV with the tensile strength of free films (thin strips) of adhesive; Part V with adhesion in glued wood joints; Part VI gives a very brief account of solvents and swelling agents for organophilic adhesives.

The work contained in both these appendices is left unfinished, owing in one case to the death of Professor Schryver, and in the other to the transference of Professor McBain to Stanford University. It is sincerely to be hoped that the work will be continued in some way. The problems of Appendix III, especially, involve for their complete solution apparatus and technique which usually can be obtained only in such laboratories as the National Physical or the Bureau of Standards. For example, one of the most interesting tentative conclusions, both from a theoretical and practical standpoint, is that "the thinner the film the stronger the joint"; but the methods of measuring the thicknesses of these films, of preparing the plane surfaces of the testing pieces, and of ensuring a complete film of adhesive, present problems of great technical difficulty.

This third report is an excellent testimonial to the value of the work sponsored by the Adhesives Research Committee.

D. C. JONES.

Periodisches System, Geschichte und Theorie. By E. RABINOWITSCH AND E. THILO. 302 pp ; 50 figs.; 49 tables Stuttgart: Verlag von F. Enke, 1930.

The theory of atomic structure has reached in the researches of Bohr, Heisenberg, Pauli, Russel, Saunders, and Hund a certain stage of development which makes it profitable to review the fundamental principles of chemistry and to discuss the most important aspect of chemistry,—the periodic system of the elements. This task the authors set themselves in this volume, and be it said at once they have been eminently successful. Their discussions are very lucid and it is a pleasure to read their book. The reviewer enjoyed the examination of this treatise so much that he only regrets that the authors have been forced, probably on account of length of space available, to abbreviate the treatment of certain topics which it would have been a pleasure to see discussed in their vivid and logical style. However, the volume is intended to be a textbook rather than a complete treatise on the subject. Students who approach the topics discussed for the first time will find that every paragraph is of importance and in some instances they will have to supplement their reading by reference to other works or to the original literature. However no extensive literature references are given, although the names of investigators who have made important contributions to the modern study of atomic structure theory are mentioned throughout the text. The treatment is quite "non-mathematical" and for this reason some of the beauty of development and deduction is lost at times. The authors bravely attempt to discuss modern quantum theory on a minimum of mathematical treatment and they succeed remarkably well. However, it seems that a student desirous of a complete understanding of "wave mechanics" will be by necessity be forced to go into the mathematical treatment of the subject.

The book is divided into five parts. Part I, "History of the natural system of the elements," begins with a review of the philosophical ideas of the ancients and traces the development of the atomic theory and the progress made in the systematic study of the elements culminating in the periodic system as known today. Part II, "The building stones of the atoms," contains a brief discussion of the electrons, the proton and the atomic nuclei and atomic numbers. Part III, "The model of the atom," deals with the part spectroscopy has played in the development of modern notions of the atom. The treatment given modern spectroscopic theory is excellent The arrangement of the spectrum lines into series, the simplification produced by the introduction of terms etc. are all dealt with in a satisfactory manner. The Bohr hydrogen atom model forms of course the background of the discussion. Its extension to many electron atoms, the shell model of the atoms, x-ray spectra, the empirical arrangement of terms, selection principles, the need for four quantum numbers for a complete description of the energy state of an electron, the Pauli principle, the formal model of an atom with several valency electrons and the wave mechanical model of the atom are developed in this section. Part III is the longest section (100 pages) of the book and contains material every chemist should be familiar with. The next portion of the book, (Part IV) "The development of the periodic system," shows the construction of the various elements as far as the arrangement of the electrons into various shells or states is concerned and it also gives the normal state of the element in the modern notation. Part V, "The periodicity of chemical properties," contains a discussion of chemical valency, ionic and atomic binding, the Haber-Born cycle, ionization potentials, electron-affinities, forces acting between ions, ionic radii, lattice energies, and Heitler-London theory of non-polar valency.

It is seen that only the simpler structures are treated. The coördination compounds, which form a very large class of substances, are not dealt with.

The systematic arrangement of the electron structures of the elements which is obtained from spectroscopic theory evidently appeals to the authors very much and the reviewer certainly shares their attitude. But in their enthusiasm they are willing to place helium in the periodic table (table 38) into the second group, because helium has the electron arrangement s^2, ^1S, which is also the arrangement for the valency shell of the alkaline earths! But the outer pair of electrons in the alkaline earths is held so much more loosely that these metals have nothing chemically in common with the rare gas-like helium! However, the reader of the book will certainly obtain a picture of the periodic table based on modern physical theory, and to chemists who wish to keep abreast of the modern development of the fundamentals of their science and to the younger generation who wishes to obtain this basic knowledge the book can be heartily recommended.

George Glockler.

L'atomistica moderna e la chimica. By M. Haissinsky, edited by U. Hoepli. 307 pp. Milan, 1930. Preface by N. Parravano, Director of the Chemical Institute of the University of Rome.

The author covers the whole field of modern atomistics from the physical and chemical angles and necessarily he must be brief within the space of the book. The treatment is therefore most concise and whenever mathematical formulation is desirable or necessary he contents himself to state relations in mathematical terms without showing their derivation from more fundamental principles. It is really astonishing that he succeeds in covering such a multitude of topics in such limited space. But he certainly does succeed, and the book gives the Italian chemist a complete view of modern knowledge and theory of atomic structure and the bearing these notions have upon chemical principles.

The twelve chapters cover the following topics: I. Molecules, atoms, and electrons. II. Thermodynamics and quanta. III. The Atom of Bohr. IV. The electronic theory of valency. V. Born's theory of grating energy. VI. Applications of Born's theory. VII. Electric charge, atomic radii, and electronic structure. VIII. Deformation of electronic orbits. IX. Photochemistry. X. Photochemical theory. XI. Catalysis and adsorption. XII. Wave mechanics and Fermi statistics. But this résumé does not give even yet all of the material covered, for each chapter consists of many subdivisions,,and it appears that no topic has been left unmentioned that may have some connection with modern atomic and molecular theory. However the Raman effect is not mentioned, although it was discovered in the year 1928.

Each chapter contains at the end a bibliography of the important articles, books, monographs, and treatises of the material covered in that chapter. An author index is appended but no subject index is included. However, the table of contents is very complete with many subdivisions and the reader should not have undue difficulty in locating a desired subject in the body of the book. While of course the same material is covered in many treatises, it will appeal to the American chemist of linguistic tendencies to study the topics involved in the Italian language.

GEORGE GLOCKLER.

Atom and Cosmos. By HANS REICHENBACH, translated by Edward S. Allen. New York: The MacMillan Company, 1933. Price: $2.00.

In our present state of turmoil in science, and in physics in particular—where discoveries quickly follow discoveries, new theories supersede each other in rapid succession, and contradictions are the order of the day—it is refreshing to find a book in which the fundamental conceptions at issue are so clearly discussed.

In as simple language as is consistent with such a difficult problem, Professor Reichenbach, who holds the chair of Natural Philosophy in the University of Berlin, gradually develops his subject, and shows, first, that it is not merely a "mania for speculation" nor a disagreement upon facts between different observers that has led to the present crisis. Its roots go far deeper, and what is at stake is no less than a revolution of our entire conception of the cosmos, involving a making over of philosophy, and a revolution as far reaching in its consequences as Copernicus' break from the Ptolemaic and Aristotelian doctrines

First giving us an insight into the world ot the astronomer, the world of space and time, and of great dimensions, then, with the aid of a ray of light and its electrical interpretations, leading us into the realm of atomic physics with its minute dimensions but immense forces, Professor Reichenbach, in a final summing-up, discusses the bearing of all this upon our philosophy of science. It is shown that ours is a world of mediocrity; that our "laws" of nature are laws only insofar as they apply to a world of moderate dimensions; that these laws which give us a semblance of certainty are in reality neither immutable nor even "true," but only practically so, by virtue of the fact that they represent statistical averages of a gigantic number of separate entities. In the microcosmos, the world of the atom, there are no such concepts as certainty or causality, while in the macrocosmos, in interstellar space, there is not that geometrical simplicity of Euclid which we formerly ascribed to it.

Perhaps one of the best features of the book is that the author develops his argument by actually following the line of reasoning of the physicist and the mathematician, and makes use only sparingly of that now so popular device of analogues, which, though unquestionably simpler and more gratifying to the uninitiated, is so often misleading as well.

As a guide into contemporary scientific philosophy this volume of Professor Reichenbach is one of the very best that has come to this reviewer's notice. The English translation by Professor Edward S. Allen of Iowa State College, maintains throughout a high degree of excellence. The only slip that I have been able to find is on p. 202, where reference is made to the *American* physicist, C. T. R. Wilson.

As stated in the preface the book is an outgrowth of a series of lectures broadcast by the author in Berlin during 1929–30. One must admire equally the skill with which Professor Reichenbach has adapted his presentation to such needs, and the courage of the broadcasting station in unleashing such material on the public, and wish that we could do the same with our enlightened populace.

W. J. LUYTEN.

Signals from the Stars. By George Ellery Hale New York: Charles Scribner's & Sons.

This little book, by Dr. Hale of the Mt Wilson Observatory, is the fourth in a series of recent aspects and achievements in astronomy. It deals particularly with the possibilities of large telescopes and with the phenomena of the solar atmosphere

Dr. Hale's own contribution to the science and the large share he has had in the planning and organizing of astronomical research accord him an undisputed authority in these fields; from his previous books the lucidity of his style is too well-known to need further comment.

An interesting dissertation on lenses precedes the discussion of giant modern telescopes; a chapter follows which deals especially with the observations of the sun's atmosphere and the correlation between solar and terrestrial magnetic phenomena. The last part of the book is devoted to a description of how the proposed 200-inch telescope might be built, and what it is hoped might be accomplished with it.

Not the least attractive part of the book is formed by the selection of photographs and illustrations. In particular this reviewer was struck by the remarkable photograph at the end which so clearly shows the distance effect in the recessional velocities of spiral nebulae.

W. J. Luyten.

Moderne Physik. Sieben Vortrage uber Materie und Strahlung. By Max Born. 24 x 16 cm.; vii + 272 pp. Berlin: Julius Springer, 1933. Price: unbound, 18 RM.; bound, 19.50 RM.

In 1932 the Technische Hochschule of Berlin and the Elektrotechnische Verein, considering that the remarkable recent developments of physics were of great interest, and might be of great importance, to electrical engineers decided to arrange a series of lectures which should describe these developments in a way generally intelligible to the technical men in question They were fortunate enough to obtain Professor Born, of Gottingen, who is well-known to all English physicists and physical chemists for his work on the solid state and on the new quantum mechanics, as the expositor, and the book before us is based on the seven lectures which he gave, the matter of those lectures having been worked up and prepared for the press by Dr. Fritz Sauter.

Obvious difficulties of the task which Professor Born set himself are the selection of the matter and the rendering of it in a form understandable without profound mathematics, especially such developments as the principles of wave mechanics and the new types of quantum statistics known by the names of Bose-Einstein and Fermi-Dirac. The selection is very properly dictated by Professor Born's particular interests, but fortunately they cover the most important aspects of modern quantum theory, and there is a large and fashionable school which will maintain that, as the title of the book implies, this is all that matters in modern physics. The presentation is, considering the nature of the subjects, extremely clear and free from difficult mathematics, all detailed calculations being relegated to an appendix, where they are carried through with elegance and with freedom from the more troublesome mathematical technique

It must not be understood that the book is altogether easy reading for a student without previous acquaintance with the subject, but it should present no insuperable difficulties to those who have a moderate knowledge of the old dynamical theory of gases, and have read some good general account of atomic structure. It is from the kinetic theory of gases that the author, naturally enough, sets out, laying stress on the nature of the assumptions. He then proceeds to deal with the elementary particles, and with the wave-corpuscle dilemma, dichotomy, duality—call it what

you will. This leads on to the Bohr atom, and its insufficiencies, which the matrix mechanics and wave mechanics have, as briefly described, so substantially reduced. The explanation of doublets and other features of the spectrum by the spinning electron and Pauli's exclusion principle occupy the fifth chapter. The stage is then prepared for a discussion of the modern systems of statistics, with the difficult conception of a degenerate gas, which has proved so valuable for the theory of the conduction of electricity in metals, even if superconductivity still defies the theorists. This part of the book in particular reveals the master, the relation of the two new systems of statistics to one another and to the older Planck and Boltzmann statistics being exposed about as well as could possibly be done in so restricted a space. The final chapter contains a general discussion of the problem of chemical combination as seen by the modern physicist.

There is ample evidence of the care which Dr. Sauter has devoted to his task of revision. In short, the book gives a beautifully balanced summary of some of the most fascinating developments of modern theoretical physics.

E. N. DA C. ANDRADE.

Lipoide und Ionen. By DR. A. DEGKWITZ. 15.5 x 22 cm.; xvi + 323 pp. Dresden and Leipzig: Steinkopff, 1933. Price: bound, 29.20 M.; unbound, 28.0 M.

This volume contains a somewhat general but very readable account of the properties of surface films and the action of the forces responsible for surface tension in effecting a molecular orientation as well as affecting chemical equilibria at interphases. In addition the more important properties of hydrophobic and hydrophilic colloidal systems are discussed

The particular value of the book lies in the fact that the author has been at some pains to collect and sift the information available on the lipoids. It has, of course, long been a matter of dispute whether the physical functions of biological lipoids are merely to form a lipoid layer possessing all the properties entailed in the acceptance of the hypothesis of Overton and Meyer in respect to cell permeability and narcosis. In many cases these layers must be reduced to the dimensions of monolayers, and in those cases their specific and peculiar properties would appear to be of little value in accounting for the observed phenomena No detailed examination of the effect of lipoids on proteins in the gel state appears to have been made, but the author has collected together the results of the experiments of Calabek, Meyer, and especially Bamberger on lecithin and cholesterol which appear highly significant. Of recent years the problem of swelling and contraction of amphoteric hydrophilic colloids, such as the proteins in the gel state, has attracted more attention and there is little doubt that the conditions of equilibrium envisaged by Procter and Loeb, namely those determined by the establishment of a Gibbs-Donnan equilibrium, is but part of the story. The restraint placed upon the system expanding on account of the differential osmotic pressure on this theory lies in the inherent extensibility of the network. The work of Astbury and Jordan Lloyd and others has shown that extensibility in solution is determined by the number and nature of the cross linkages, as well as by the balance between the hydrophobic and hydrophilic portions of the polypeptide chains. Increasing the number of cross linkages or decreasing the hydrophilic portions of the chain renders the extensibility in solution less. This is the variable not considered in the formal mathematical investigation. We know thanks to the work of Kruyt and of Katz, that numerous substances whether ions or organic molecules are adsorbed by the proteins and affect the balance between the hydrophobic and hydrophilic portions of the molecule; thus tannic acid or amyl alcohol reduce the hydrophilic character, whilst thiourea and iodoacetic acid increase the number of hydrophilic groups We may regard these substances in the terminology of the biologist as antagonistic to each other. It appears from an examination of the data presented by the author that lecithin behaves in a manner similar to thiourea, i.e., it is a hydrophil donator, whilst cholesterol is a hydrophobe donator. A mixture of the two preserves an adjusted equilibrium. If this really be the case the way is paved for the interpretation of many phenomena such as the production of hemolysis by varied reagents.

Eric K. Rideal.

SURFACE ACTIONS OF SOME SULFUR-BEARING ORGANIC COMPOUNDS ON SOME FINELY-GROUND SULFIDE MINERALS

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The fine grinding required to liberate ore minerals so as to permit the fullest application of mineral separation by flotation produces particles of all sizes, from those having a diameter of about 100 microns to those of truly colloidal dimensions. The surface area of the solid phases is large in relation to their bulk, so that actions taking place at the interface between the solids and the liquid in which they are immersed may involve a substantial amount of the agent in question, even though the action—or reaction—does not proceed on the solid to a depth greater than that corresponding to one or two atomic diameters. The physicochemical effect of these reactions on mineral surfaces is known to be tremendous: indeed many of the actual reactions have been surmised from observed physicochemical phenomena.

The action (on the mineral surfaces) of the organic compounds that promote attachment of minerals to gas bubbles is of particular interest to the student of physical chemistry, as the discovery of the actual *modus operandi* may have applications in many fields of colloid chemistry not directly related to flotation. Establishment of the mode of action of these organic compounds—generally called collectors—on the minerals is, of course, of paramount interest to the flotation engineer.

While it is generally acknowledged that collector molecules, being heteropolar, adhere to the mineral surface with their hydrophobic ends oriented away from the mineral, the mechanism of this attachment has been until quite recently a matter of speculation.

The simplest collectors are possibly the fatty acids and their alkali soaps, which are used principally in the flotation of non-sulfide minerals. More complex organic compounds whose molecules contain sulfur, nitrogen, or phosphorus are used for the flotation of sulfide minerals and of the oxidized minerals of lead and copper.

Finely ground apatite[1] abstracts a considerable quantity of palmitate ion from an aqueous solution of sodium palmitate, while quartz does not act in this manner. Although quartz sometimes appears to be floatable with sodium oleate as the collector, it has been shown (1a) that flotation takes place to a substantial extent only when quartz has been activated by a cation, such as Pb^{++}, Zn^{++}, Ba^{++}, Ca^{++}, or Fe^{+++}, which is capable of forming an insoluble soap. The fact that oleate ion, as such, adheres only to surfaces that have cations capable of forming insoluble oleates suggests that the mechanism of the abstraction is chemical. The action is practically irreversible and does not take place in accordance with the Freundlich adsorption isotherm (2).

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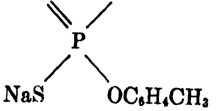
[1] Calcium phosphate in which some phosphate is replaced by fluorine or chlorine; the formula is often stated to be $Ca_5(F, Cl)(PO_4)_3$.

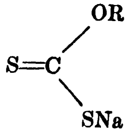
The behavior of some sulfur-bearing collectors, such as xanthates, toward oxidized lead and copper minerals is also well known (1b). These substances react metathetically with the surface of the mineral, forming thereon heteropolar coatings with the water-repellent end of the molecules of the coating oriented toward the water (3).

The mechanism of the action of the sulfur-bearing collectors (e.g., thioureas, mercaptans, thiophenols, or xanthates) on sulfide minerals is less accessible to investigation, and apparently more complicated, than the action of fatty acids and soaps.

In spite of the evidence adduced by Taggart and his associates (4) of the strictly chemical character of the reaction between some collectors and some sulfide minerals, there are investigators who still adhere to the view that the phenomenon is one not involving primary valence forces. Holman (5), for instance, favors the secondary valence theory of adsorption, in that he assumes that xanthate molecules or ions are oriented at the mineral surfaces so that the double-bonded sulfur atoms, which he considers to be air-avid, are away from the mineral surface. Ostwald (6), on the other hand, considers that it is the double-bonded sulfur atom which has an affinity for the mineral, and at least in the case of sodium dicresyl dithiophosphate ("aerofloat"),



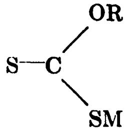
and with xanthates,



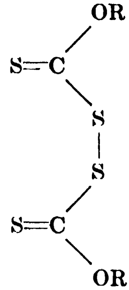
that it is the hydrocarbon group that is hydrophobic. The majority of investigators are in accord with this latter opinion. But Ostwald goes further and imagines that a collector must be "triphilic," that is, that each of its molecules must have a water-avid group, an air-avid group, and a mineral-avid group. Ostwald appears to support the view that the adherence of the reagent is a matter of residual valence.

With those who believe that the abstraction of reagent from solution or suspension by the mineral is the result of a chemical reaction, it is still a question whether the major reaction is with the mineral itself, or with a mineral surface that has become oxidized (Taggart and coworkers), and whether it is the reagent itself, or a product resulting from the oxidation or decomposition of the reagent, which reacts with the mineral.

An investigation of the action of xanthates,



and of dixanthogens,



on galena and pyrite has been conducted at the Montana School of Mines. Work is now in progress in which experimentation is conducted with a wider variety of minerals and reagents.

THE SURFACE REACTIONS OF XANTHATES AND DIXANTHOGENS ON GALENA

In regard to the action of xanthate on galena it is known (3) that: (a) the surface of galena oxidizes rapidly in the presence of moist air or of water exposed to air, to form a film of lead sulfate, basic lead sulfate, or a compound of lead, sulfur, and oxygen of indeterminate composition containing less oxygen in relation to sulfur than the sulfate or basic sulfate; (b) this oxidized coating penetrates cleavage planes to an unknown but substantial extent; (c) the oxidized coating reacts with alkali xanthates, forming lead xanthates, which are less soluble in water than lead sulfate or basic lead sulfate; (d) slightly oxidized galena abstracts xanthate ion from solution and yields sulfate and other anions in approximately equivalent amount.

It was proposed to investigate further the action of xanthates on galena with particular reference to the effect of oxidation on the reaction products. In most cases the galena was finely ground, so that the final surface area of the mineral particles was several hundred times the original area. This made possible the recovery of sizable amounts of reaction products from quantities of galena that were not excessively large. The reaction products were recovered from the mineral by leaching with carefully purified acetone or benzene. The solvent was then evaporated quickly with a fan, so as to prevent as far as possible decomposition of the solute while in solution. Lead xanthates, particularly the higher xanthates and the branching or secondary compounds, are prone to decompose in solution, especially if warm; consequently any method of concentrating the leach liquor by the application of heat, such as distillation, is out of the question.

The raw galena was a jig concentrate from the Tri-State district. Before cleaning (see below) the galena was crushed, concentrated by tabling, and sized to 20/65 mesh by screening. After this preliminary purification the impurities were iron oxides and sphalerite, together with minor amounts of pyrite, calcite and silicates. Of these the ferric oxides were suspected of being the most harmful. However, their removal in the subsequent cleaning step was almost complete.

After the preliminary cleaning just described, the galena was cleaned with an ammonium chloride–hydrochloric acid solution and with 0.5 *N* redistilled hydrochloric acid. The pH of the ammonium chloride–hydrochloric acid stock solution was 1.4, but before use the solution was diluted with thrice its volume of distilled water; a much greater concentration of cleaning solution results in undue metathesis of the hydrochloric acid with the galena, and in precipitation of salts on the mineral.

The galena was washed with distilled water until the rinse was clear, then boiled gently for four hours in 400 cc. of the diluted ammonium chloride–hydrochloric acid solution. The operation was repeated until examination with a binocular microscope showed the galena to be substantially free from impurities other than a little quartz, pyrite, and sphalerite; total impurities usually were about 0.3 per cent. The sample was next boiled gently for two hours with 400 cc. of 0.5 *N* hydrochloric acid, and then was washed with distilled water. The hydrochloric acid treatment and subsequent washing were repeated.

The object of this procedure was to remove the lead sulfate coating from the galena surface and to dissolve ferric impurities. This method was preferred to the use of ammonium acetate, for it was thought ammonium acetate might contain organic impurities difficult to remove. Also, hot hydrochloric acid (7) dissolves lead sulfate, especially if a large concentration of chloride ion is maintained by the addition of an alkali chloride or ammonium chloride.

After the special cleaning treatment just described, the mineral was ground in a closed porcelain jar of the type known as an assay mill. The jar was filled half-way with pebbles and pulp, the remainder of the space being occupied by air. In some tests a nitrogen atmosphere was used; this is specifically stated in every instance. Every grind was, of course, a wet grind.

It was found that galena treated in this manner abstracts almost as much xanthate after it is ground as galena that has not been cleaned. This indicates that galena almost completely reoxidizes on a few hours' exposure to air. The amount of oxygen in an assay mill is of an order of magnitude sufficient to oxidize the fresh galena surface produced by a six-hour grind.

The following experiments were singled out from among many as of especial significance in ascertaining the true action of xanthates and dixanthogens on galena.

Experiment No. 1

Five hundred grams of cleaned galena was ground for six hours in the presence of 500 cc. of water; 2.50 g. potassium ethyl xanthate was added to the pulp of ground mineral. The mixture was stirred, allowed to stand for fifteen minutes and filtered. It was found by titration that approximately 1.0 g. of the reagent remained in the filtrate in the form of potassium ethyl xanthate; in other words, ethyl xanthate ion corresponding to 1.5 g. of molecular potassium ethyl xanthate had been abstracted or decomposed.

After dewatering, the treated mineral was leached with nearly one liter of acetone; about one-half of the acetone was stirred with the mineral for fifteen minutes, and the mixture was filtered, and the rest of the acetone was used in washing the filter cake. The filtrate was evaporated with an electric fan. During the process characteristic crystals of lead xanthate (8), arranged in lily-pad fashion, appeared on the surface of the leach liquor. Besides the lead xanthate, there was found in the leach residue some oil, possibly ethyl dixanthogen, and a trace of lead sulfide, but no potassium ion. Methods of identification of these and other leach residues are presented elsewhere (8).

This experiment was repeated, except that 1.50 g. of xanthate was used in place of 2.50 g. Only 0.22 g. of potassium xanthate was found in the aqueous filtrate, hence 1.28 g. was abstracted by the mineral. The dewatered, treated mineral contained the same substances as before.

This experiment was again repeated, except that the amount of xanthate was reduced further to 1.0 g., and that the grinding time was increased to eight hours. All the xanthate was abstracted. The dewatered, treated mineral contained the same substances as before.

These experiments show that xanthate ion corresponding to one gram or more of potassium ethyl xanthate is abstracted in fifteen minutes by

500 g. of galena ground from six to eight hours in contact with a limited volume of air. These experiments also show that a considerable excess of xanthate ion is required to increase greatly the amount abstracted.

Experiment No. 2

Experiment No. 1 was repeated, except that the grinding time was increased threefold to eighteen hours. Of 2.50 g. of potassium ethyl xanthate added initially, but 0.42 g. remained in the aqueous filtrate, indicating that xanthate ion corresponding to 2.08 g. of the agent had been abstracted or decomposed. In this case the amount of xanthate abstracted did not increase in proportion to the added surface produced by the longer grind (9). This is perhaps because some of the freshly produced surface was not completely oxidized, and therefore did not react to the extent that a completely oxidized surface would react.

Experiment No. 3

Five hundred grams of cleaned galena was ground for eighteen hours in the presence of 1.00 g. of potassium ethyl xanthate. The xanthate ion disappeared completely. However, the amount of lead xanthate recovered from the treated mineral was very small. In this case the xanthate had apparently decomposed, either while in the solution or while at the mineral surface as solid xanthate. In this, as in other tests in which the mineral was ground in the presence of the reagent, various decomposition products were noted, especially an oil, possibly ethyl dixanthogen, and elemental sulfur, and perhaps lead ethyl mercaptide (8).

This test shows that potassium ethyl xanthate or lead ethyl xanthate decomposes much faster if in association with a galena surface, moisture, and atmospheric gases than if in bulk in the solid state or in pure aqueous solution or suspension.

Experiment No. 4

Five hundred grams of cleaned galena was ground four hours and then treated with 2.00 g. of potassium *n*-amyl xanthate, in place of ethyl xanthate. Lead *n*-amyl xanthate was the chief product extracted by leaching the mineral.

This test shows that the primary reaction between dissolved xanthate and galena is the same whether *n*-amyl or ethyl xanthate is used.

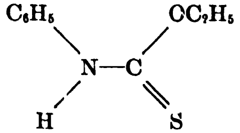
Experiment No. 4a

Experiment No. 4 was repeated except that the amount of xanthate was reduced to 1.00 g., and that, after treatment, the mineral was exposed in aqueous pulp to the atmosphere for a day before filtering. As the galena was unusually dry after this treatment, it was leached with benzene instead of acetone. Sulfur corresponding approximately to one sulfur atom per xanthate molecule abstracted was the only product identified; however, a strong odor suggestive of a mercaptan or of a xanthic ester was noted.

These tests show that lead amyl xanthate decomposes rapidly, and in a well-defined way, when in contact with lead sulfide, moisture, and air.

Experiment No. 4b

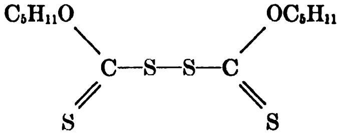
Experiment No. 4a was repeated with phenyl thiourethan,



used in place of xanthate. Sulfur corresponding to approximately one atom per molecule of reagent was obtained in the leach liquor.

Experiment No. 5

One hundred grams of uncleaned galena, ground thirty hours with 400 g. of granite in the presence of *n*-amyl dixanthogen,

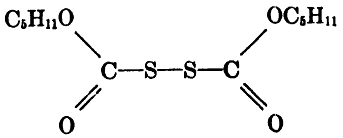


was floated, filtered, and then leached with benzene. The benzene left a residue of sulfur plus some volatile material, possibly the amyl ester of amyl xanthic acid (8). The amount of sulfur recovered was approximately that which would be contributed by two of the sulfur atoms in each dixanthogen molecule.

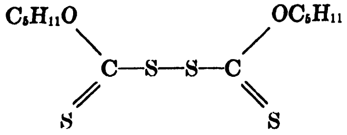
This test shows that dixanthogen, which is the direct oxidation product of xanthate, is itself decomposed when allowed to remain in contact with a large amount of galena surface.

Experiment No. 5a

If amyl formate disulfide,



be substituted for amyl thioformate disulfide (amyl dixanthogen),



sulfur appears again as the only solid reaction product. The amount of sulfur obtained is again approximately that corresponding to two sulfur atoms per molecule of reagent, showing that in this case, as probably in that involving dixanthogen, the sulfur left with the mineral after reaction is the single-bonded, or disulfide, sulfur.

Experiment No. 6

Seven hundred grams of uncleaned galena was ground for four hours in an atmosphere of nitrogen in the presence of 1.00 g. of potassium ethyl xanthate which had been added in oxygen-free solution. The assay mill was emptied in a nitrogen atmosphere, and the slime was filtered and washed with acetone, also in an atmosphere of nitrogen.

The aqueous filtrate was titrated immediately for xanthate. It was found that xanthate ion corresponding to 0.99 g. of the reagent had disappeared. Sulfate ion was found in the aqueous filtrate, and lead xanthate was recovered from the treated mineral.

A similar experiment was conducted with cleaned galena in a nitrogen atmosphere. Again a substantial disappearance of xanthate ion was noted. Xanthate disappearance, sulfate evolution, and lead xanthate extraction from the mineral were much smaller in this experiment than in corresponding experiments conducted in air.

Taken as a whole these experiments confirm the view of Taggart and his associates, in so far as galena and xanthates are concerned, that the reaction is essentially a metathesis between oxidized coatings on the mineral and the xanthate in solution, although they do not exclude the possibility of reaction between galena itself and the xanthate in solution.

From the experiments described in this paper, it would appear that the following reactions take place:

1. Galena + oxygen → lead sulfate coating on galena
2. Galena coated with lead sulfate + potassium xanthate in aqueous solution→ galena coated with lead xanthate + potassium sulfate in solution
3. Lead xanthate coating on galena + oxygen (?) → dixanthogen coating on galena + oxidized lead salt.
4. Galena not coated with lead sulfate + dixanthogen suspended in pulp → galena coated with dixanthogen
5. Dixanthogen coating on galena + oxygen (?) → elemental sulfur corresponding to the two single-bonded (disulfide) atoms of sulfur per dixanthogen molecule + volatile sulfur organic compounds (xanthic esters and mercaptans?).

The reactions are purposely not formulated because of the uncertainty which at present surrounds some of them. It appears that steps 2 and 5 are relatively rapid, that 3 is rather slow, and that the speed of 4 depends on physical rather than chemical circumstances.

THE SURFACE REACTIONS OF XANTHATES AND DIXANTHOGENS ON PYRITE

From what is known concerning galena it is tempting to conclude that similar reactions take place with other sulfide minerals. In the case of pyrite, however, it is difficult to postulate the formation of iron xanthate as a first step in a chain of reactions because ferrous xanthate is quite soluble[2] and because ferric xanthate hydrolyzes to ferric hydrate and xanthic acid.

Since, however, xanthates are very effective in floating pyrite, and since xanthates are abstracted by the mineral, it is evident that xanthate ion or some decomposition product must attach itself to the surface of the mineral. The most probable substance seems to be dixanthogen. The experiments described in the following pages, however, indicate that the reactions involved are somewhat more complicated than is implied by the view that the active collector is dixanthogen.

The experimental procedure for testing pyrite was essentially the same as that used in Experiment No. 1, in which galena was used. The pyrite was hand-picked mineral from Butte. After being cleaned it contained a trace of arsenic, less than 0.05 per cent copper, and no zinc.

The pyrite was cleaned with 1:1 hydrochloric acid according to the method recommended by C. W. Orr (12) except that the mineral was first washed, at a coarse size, with redistilled acetone. This step was designed to remove oily compounds possibly deposited from suspension in air while the mineral was stored in the laboratory (3). Unless otherwise stated, the experiments were performed in air and a 500-g. sample of pyrite was used in each case. All the grinds were wet grinds; during grinding the pulp dilution was 1:1.

Experiment No 7

To 20/65 mesh cleaned pyrite ground for eight hours was added 1.00 g. of potassium ethyl xanthate. Immediately after the addition of xanthate there was an odor resembling that of commercial carbon disulfide. The xanthate was completely abstracted or destroyed. The aqueous filtrate contained ferric ion, chloride ion, sulfate ion, but no sulfide ion.

The acetone leach liquor contained elemental sulfur.

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[2] The solubility of ferrous ethyl xanthate exceeds one part per thousand, whereas the solubility of lead ethyl xanthate is less than one part per million.

Experiment No. 7a

Experiment No. 7 was repeated, except that the pulp was allowed to stand in the assay mill for two days before opening the mill. A much stronger vacuum than usual was noted on opening the mill. This indicates that the freshly produced pyrite surfaces, the reagent, or both had been more completely oxidized by the oxygen in the mill than if the mill had been opened immediately.

Besides sulfur, the following substances appear to have formed during the reaction:—carbon dioxide, carbon disulfide, carbonyl sulfide, and a relatively complex organic acid (8).

These experiments show that potassium ethyl xanthate is abstracted by pyrite ground in a limited volume of air, from a pulp slightly acid in the vicinity of the mineral particles, probably because of oxidation of the pyrite, to yield principally elemental sulfur, but also miscellaneous volatile organic compounds as yet incompletely determined.

Experiment No. 8

Acid-cleaned pyrite was ground eighteen hours with 2.00 g. of potassium *n*-amyl xanthate. The aqueous mixture was agitated with redistilled benzene in a closed jar, on agitating rolls. All the pyrite went into the benzene phase. The benzene was evaporated with a current of air; the resulting residue contained sulfur and something that smelled like an ester.

This experiment shows that the reactions with amyl xanthate are similar to those with ethyl xanthate.

Experiment No. 9

Five hundred grams of cleaned pyrite and 1 g. of ethyl dixanthogen in 20 cc. of ethyl alcohol was added to one-half liter of water. The mixture was ground for six hours. The mill was opened and a sample of the pyrite, which formed a dry froth (14), was immediately shaken with ether and the sample was tested for dixanthogen. No dixanthogen or xanthate was found,—only sulfur. The amount of sulfur recovered from the total pulp was 0.210 g., which corresponds nearly to two atoms of sulfur per dixanthogen molecule.

This experiment shows that dixanthogen in contact with pyrite is decomposed to yield elemental sulfur.

Experiment No. 10

Five hundred grams of pyrite was ground twelve hours in a normal potassium hydroxide solution. After this preliminary grind 1 g. of ethyl dixanthogen was added and the mixture was ground further for eight hours. The leach liquor contained some oil, possibly dixanthogen, together with sulfur. The sulfur was less abundant than in experiments conducted in pulps not made alkaline.

This experiment suggests that if the sulfuric acid formed by the reaction of atmospheric oxygen with pyrite in the presence of water is neutralized and an excess of alkali is present, the dixanthogen may not decompose so readily, nor perhaps be abstracted so readily.

Experiment No. 11

Five hundred grams of cleaned pyrite was ground for six hours to be tested as a blank. In the acetone leach there was found a small amount (less than 0.020 g.) of sulfur and traces of ferric chloride. The amount of sulfur found was less than one-tenth the amount found in corresponding experiments with a xanthate or dixanthogen.

This experiment shows that the sulfur observed in experiments 7 to 10 is essentially not an impurity derived from the mineral.

Experiment No. 12

Seven hundred grams of uncleaned pyrite was ground in a nitrogen atmosphere to parallel experiment No. 6 carried out with galena, except that amyl xanthate was used in place of ethyl xanthate. Of the 0.991 g. of xanthate added, 0.986 g. was abstracted or decomposed. Less sulfur was found than in other experiments, and the sulfur was sticky with an oil.

This experiment shows that amyl dixanthogen is formed when amyl xanthate is added to pyrite, but that the dixanthogen is subsequently decomposed to yield sulfur.

From the above experiments it is clear that the product of the reaction of a xanthate with pyrite, or of a dixanthogen with pyrite, is in the end sulfur, together with some as yet incompletely identified volatile compounds. If the quantity of oxygen or other oxidizing agent is minimized, the reaction chain may be limited merely to the production of dixanthogen.

It is not known whether xanthate ion is adsorbed momentarily at the pyrite surface where it becomes oxidized to dixanthogen, or whether soluble iron salts are responsible for the change of the xanthate in solution. In the absence of definite evidence as to the mode of oxidation of the xanthate, the following reaction steps appear likely:

1. Pyrite + oxygen + xanthate ion → dixanthogen-coated pyrite + sulfate ion;
2. Pyrite + dixanthogen suspension in water → dixanthogen-coated pyrite;
3. Dixanthogen-coated pyrite + oxygen → sulfur + miscellaneous volatile compounds.

THE SURFACE REACTIONS OF OTHER SULFIDE MINERALS

Preliminary experiments in need of duplication and extension have been conducted with chalcocite, Cu_2S, chalcopyrite, $CuFeS_2$, and sphalerite, ZnS. In view of the interest presented by these incomplete experiments, some of the results are presented here.

Sphalerite does not abstract xanthates from solution (1d); no reaction product can be extracted from the mineral.

Chalcocite abstracts isoamyl monosulfide from aqueous suspension. Part of the reagent, unchanged, can be extracted from the treated mineral.

Chalcocite abstracts isoamyl disulfide from aqueous suspension. The reagent is changed to the monosulfide and sulfur.

Chalcocite abstracts isoamyl mercaptan from aqueous suspension or solution. The reagent appears changed to isoamyl monosulfide and sulfur (13).

Chalcopyrite abstracts isoamyl monosulfide from aqueous suspension. The reagent appears changed to a mixture of sulfur and an oily substance as yet unidentified.

SUMMARY

Much work remains to be done to complete the investigation which has been undertaken. However, the following conclusions summarize the results obtained so far.

1. Galena reacts with xanthates to form lead xanthates, principally by metathesis of oxidized coatings with the xanthate. Subsequently the xanthate changes to sulfur and unidentified oils. Some of the changes appear to require atmospheric oxygen. Because of the great area over which the lead xanthate or dixanthogen is assumed to be spread, the galena may well be regarded as a catalyst in the decomposition of the primary reaction product.
2. Galena abstracts dixanthogen from aqueous suspension, and apparently catalyzes the decomposition or oxidation of the dixanthogen to yield principally elemental sulfur.
3. Pyrite, or ferric ion derived from it by oxidation, changes xanthate to dixanthogen; the dixanthogen can be extracted from the mineral surface provided oxidation of the dixanthogen is prevented.
4. If oxidation at the surface of pyrite is not restricted, the dixanthogen formed there by preliminary oxidation of xanthate, or that abstracted directly from a suspension of dixanthogen, breaks down to elemental sulfur and miscellaneous volatile compounds.
5. Reactions of the copper and zinc sulfides appear to be different from those of galena and pyrite. In general, indeed, it may be said that each mineral-reagent combination requires a special investigation.

The writers wish to express their appreciation to Mr. M. S. Hansen and Mr. L. J. Hartzell, Jr., for the use of unpublished data.

REFERENCES

(1) Gaudin, A M Flotation McGraw-Hill Book Co, New York (1932) (a) p 361, (b) pp 64, 296, 308, (c) pp 65–6, (d) p 205

(2) Luyken, W, and Bierbrauer, E Flotation in Theory and Practice Julius Springer, Berlin (1931)

(3) Taggart, A F, Taylor, T C, and Knoll, A F Am Inst Mining Met Engrs, Milling Methods, p 223 (1930) Chemical Reactions in Flotation

(4) Taggart, A F, Taylor, T C, and Ince, C R Am Inst Mining Met Engrs, Tech Pub No 204 (1929) Experiments with Flotation Reagents

(5) Holman, B W Trans Am Inst Mining Met Engrs, p 613 (1930) Flotation Reagents

(6) Ostwald, Wolfgang Kolloid-Z **58**, 179 (1932) On the Theory of Flotation

(7) Mellor, J W Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol VII Longmans, Green and Co, New York (1927) (See "lead sulfide," also 'galena")

(8) Wilkinson, W D Master's thesis, Montana School of Mines, 1932 Certain Sulfur-Bearing Flotation Collectors and Their Reactions with Sulfide Minerals

(9) Gross, John, and Zimmerley, S R Am Inst Mining Met Engrs, Milling Methods, p 30 (1930)

(10) Norris, James F Organic Chemistry, p 240 McGraw-Hill Book Co, New York (1922)

(11) Shcherbakova, E A Tzvetnuie Metalli, **1932**, 8 Xanthates, their Properties and Importance for Flotation

(12) Gaudin, A M, Glover, Harvey, Hansen, M S, and Orr, C W Flotation Fundamentals, University of Utah Tech Paper No 1, 1928

(13) Slagle, Kenneth H, and Reid, E Emmet Ind Eng Chem **24**, 448–51 (1932) Action of Some Mercaptans in Hydrocarbon Solution on Copper and Copper Sulfide

(14) Gaudin, A M, and Malozemoff, P J Phys Chem **37**, 597–607 (1933) Recovery by Flotation of Mineral Particles of Colloidal Size

FREEZING POINTS AND OSMOTIC PRESSURES OF LACTOSE SOLUTIONS

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In what ratio of equivalence lactose may be substituted for sucrose in solutions in which the essential effect of the sugar present is dependent on osmotic pressure, is the question this work was undertaken to answer. Since osmotic pressure is proportional to the number of discrete units of solute in a solution, it is to be expected that anhydrous lactose would be exactly equivalent to sucrose on a weight basis, provided only that the two sugars are associated, dissociated, or hydrated in water solution to the same degree. Preliminary calculations of osmotic pressures of sucrose solutions showed that values derived by the gas law formula differ from those derived from freezing point measurements of Pickering (4) in such a way as to be explicable by the assumption of hydration of each sugar molecule by three to six molecules of water, the exact number depending on the concentration of the solution. It seemed reasonable to expect that a similar, though not necessarily identical, situation would be found to exist for lactose solutions. In any case, actual measurements were desirable.

Freezing points of lactose solutions were determined by the Beckmann method with the usual precautions. Several samples of purified lactose were used, each sample having been dried separately. The checking of results by use of different samples was taken to indicate a satisfactory degree of purity of all the samples. The lactose for each determination was weighed into a Florence flask, the required quantity of water added by means of a pipet, and the flask warmed until solution was complete, care being taken to minimize loss of water by evaporation. The solution was then transferred to the freezing tube and a freezing point determination made.

Particularly at the higher concentrations it frequently happened that crystallization of sugar would begin before freezing of water had commenced. This could be detected by the continuing rise of the mercury thread in the thermometer during separation of solid material, and could be verified by removing the freezing tube and observing whether the crystals in the solution were lactose or ice. Repeated efforts to obtain freezing points on solutions of concentrations higher than the highest recorded in the table were unsuccessful because the crystallization was initially of lactose. The values recorded in table 1 are the averages of the results of at least three determinations in each case.

TABLE 1

Freezing points and osmotic pressures of lactose solutions

WEIGHT OF ANHYDROUS LACTOSE IN 100 GRAMS WATER	FREEZING POINT Δ	OSMOTIC PRESSURE 11 898 × Δ
grams	*degrees C*	*atmospheres*
4 738	−0 280	3 33
9 452	−0 557	6 63
14 144	−0 839	9 98
18 812	−1 125	13 39
23 451	−1 426	16 96
28 567	−1 731	20 59
37 897	−2 353	28 02
47 201	−2 986	35 52
56 436	−3 672	43 68
65 594	−4 344	51 68

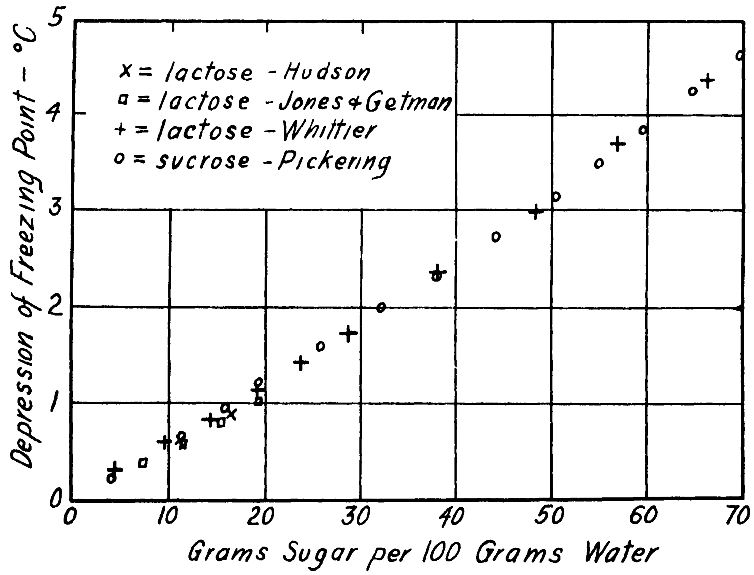

Fig. 1. Freezing Point Depressions of Solutions of Lactose and of Sucrose

The concentrations used were prepared by dissolving 5 g. or some multiple of 5 g. of lactose hydrate in 100 g. of water. These concentration values were corrected for the effect of undercooling by means of the formula

$$w_a = \frac{w}{1 - \frac{ct}{L}}$$

in which w is the weight of lactose hydrate originally present in 100 g. of water, w_a is the weight of lactose hydrate present in 100 g. of water at the moment the thermometer thread has risen to the freezing point after undercooling, t is the amount of undercooling in degrees Centigrade, c is the specific heat of the liquid in calories, and L is the latent heat of fusion of ice in calories. The concentration of anhydrous lactose was next calculated by means of the formula

$$w_b = \frac{342}{360} \cdot w_a \quad \frac{100}{100 + \frac{18}{360} \cdot w_a}$$

in which w_a has the same significance as above, and w_b is the weight of anhydrous lactose in 100 g. of water.

The factor used for calculating osmotic pressure from depression of freezing point, 11.898, is that given by Levalt-Ezerskii (3) for sucrose. The justification for applying this value to calculations involving lactose is the chemical similarity of the two compounds and the close agreement of freezing points of their solutions. This agreement is shown in figure 1, in which Pickering's (4) values of freezing points of sucrose solutions are plotted together with values for lactose by Hudson (1), by Jones and Getman (2), and by the author.

The values of osmotic pressure given in table 1 are in all cases greater than values calculated from the gas law relationship, $\frac{22.4}{342} \times 10\ w_b$, the difference being proportionately greater at the greater concentrations. Since values for lactose agree with values for sucrose within 1 per cent and since, as established by freezing point determinations on a solution containing both sugars, the osmotic pressures of the two sugars are additive, it is concluded that one may be substituted for the other in solutions without appreciable influence on osmotic effects.

REFERENCES

(1) Hudson: J. Am. Chem. Soc. **30,** 1773 (1908).
(2) Jones and Getman: Am. Chem. J. **32,** 426 (1904).
(3) Levalt-Ezerskii: J. Russ. Phys. Chem. Soc. **51,** 231 (1920).
(4) Pickering: Ber. **24,** 3333 (1891).

II. THE ADSORPTION OF THORIUM B BY THALLIUM HALIDE CRYSTALS IN THE PRESENCE OF VARIOUS IONS

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INTRODUCTION

In formulating the precipitation and adsorption rules (1) of Paneth, Fajans, and Hahn, much work has been done on the adsorption of various ions of common elements, of radioactive elements, and of dyes on silver and mercury salt crystals. Relations have been shown between adsorbability and insolubility, adsorbability and mixed crystal formation, and adsorbability and weakness of dissociation of the compound formed by the adsorbed ion. It has been our purpose to extend this study to thallium halide crystals. In this paper measurements made on the adsorption of thorium B by thallium bromide and thallium iodide crystals and the effect of various anions and cations on this adsorption will be reported.

The polar crystals of thallium bromide and thallium iodide are of the cubic system of the cesium chloride type, where a thallium ion is surrounded by eight halide ions. The surface ions in the lattice possess a residual attractive force which is available for attaching to the crystal ions which fit into the crystal lattice, or which form an insoluble or undissociated compound with the oppositely charged ions of the lattice. When thallium iodide is in equilibrium with its saturated solution, adsorption of its own ions is analogous to crystal growth. When thallium iodide crystals are in contact with a solution of an iodide salt, they take on a minus charge owing to the adsorbed iodide ions and when they are in contact with a solution of a thallium salt, they take on a plus charge owing to the adsorption of the thallium ions. If a thallium iodide crystal is in contact with its saturated solution and has a preferential adsorption for one of its own ions, the surface of the crystal will take on the charge of the ion which has been adsorbed. In the case of silver iodide, Lange and Crane (2) found that silver iodide had adsorbed iodide ion from the saturated solution and that the silver iodide–saturated solution potential was 0.004 volt. It was necessary to bring the silver iodide crystal to equilibrium with a 4×10^{-6} normal silver nitrate solution in order to neutralize this minus charge on the crystal. Bromide ion is less readily adsorbed to silver bromide crystal surfaces and chloride ion less so than bromide ion. In this series of halide ions, the adsorbability of the ions on the silver halide crystal is (1) in the inverse order of the solubility of the salts formed by the ions, (2) in the same order of the deformability of the ions, and (3) in the inverse order of the hydration of the ions. Fajans considers these three factors of prime importance in determining the relative adsorbability of similar ions.

We have found in the case of the purest thallium iodide which we could prepare that the iodide ion was preferentially adsorbed, giving the thallium iodide crystal a negative charge. This "neutral" thallium iodide crystal showed a marked adsorption for thorium B ions and in colloidal suspension migrated toward the positive terminal when viewed in the field of a microscope. In comparing the relative adsorbability of the halide ions, we found that iodide ion was more easily adsorbed than bromide ion and bromide ion more easily adsorbed than chloride ion on thallium halide crystal surfaces.

Fajans has found in the case of the relative adsorbability of dissimilar ions that other factors than those just mentioned are also of importance (3). Even though silver erythrosinate is one hundred times more soluble than silver iodide, the erythrosinate ion is much more easily adsorbed than is iodide ion on silver iodide. In this case he states that there is a dominating influence of the non-polar forces in the large dye ion. He also finds that thiocyanate ion is better adsorbed on silver iodide than is bromide ion even though silver bromide is less soluble than is silver thiocyanate.

PREPARATION OF MATERIALS

Water

Water for all the experiments was made by use of a Barnstead still. By keeping the condenser water hot, water with a conductance of 1.7×10^{-6} to 2×10^{-6} was easily obtainable. This water was stored and used in Pyrex containers which had been thoroughly steamed out. In the washing of the crystals, the water was piped directly from the block tin condenser of the still to the washing tower shown in figure 1. Thus it was possible to wash the precipitated crystals over long periods of time with pure water with no possibility of contamination by foreign ions. In the case of the silver salts used in the work to be described in the next paper, the water was run through the wall of a dark room so that the silver halide crystals could be washed continuously with agitation in the dark with water of the conductance given above.

Thallium bromide and thallium iodide

In the earlier work on the adsorption of ions on precipitates, the adsorption was allowed to take place as the precipitate was formed. For instance, to a silver nitrate solution containing thorium B ions or dye ions was added potassium bromide solution until the equivalent point was reached, or to such a point that there was a definite excess of silver ions or bromide ions. The solution was then freed from the precipitate by filtering or centrifuging and the concentration of the thorium B or dye ions was determined in the solution. Obvious possible errors could be caused by (1) the presence of the potassium or the nitrate ions, (2) the difficulty of forming the precipitate each time in such a way as to have the same surface; (3) the difficulty of preventing local excesses of either ion, which would result in local charges on the precipitate; and (4) the possibility of the occlusion of thorium B (either as ions or in some colloidal or pseudocolloidal form) or the dye ions in the precipitate.

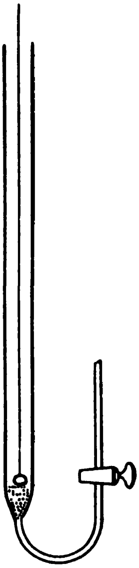

FIG. 1. WASHING TOWER

The results of such work could be treated more qualitatively than quantitatively. Beckley and Taylor used a suspension of thoroughly washed silver iodide as adsorbent. Here there is the possibility of a changing surface of the precipitate owing to small crystals going into solution and recrystallizing on large crystals. They report a change of 50 per cent adsorption in six months time. J. Walker made use of silver bromide powder, and in the latest work of Fajans (4) the crystals used were prepared as a perfectly dry powder and a definite weight was always used in the adsorption experiments. This method has the advantage of obtaining reproducible surfaces which undergo slight changes in the few minutes needed to reach the adsorption equilibrium. A large amount of powder can be prepared and preserved over a long period of time, thereby assuring the same surface per unit of weight for a number of experiments.

The thallium bromide and thallium iodide crystals were prepared by three methods in order to study the behavior of the so-called "neutral particle." Hahn (5) reports that it is possible to prepare crystals whose surfaces are electrically neutral and that such crystals have no adsorption for radioactive ions. Our crystals prepared by the three methods to be described all possessed a marked adsorption for thorium B ions.

First method. Two liters each of 0.1 *N* thallium nitrate and potassium bromide or potassium iodide were allowed to drop at equal rates into 4 liters of water contained in a large balloon flask. The water was rapidly stirred. The precipitated salt was then allowed to settle and the supernatant liquid was siphoned off. The precipitate was washed by decantation ten times with 4-liter portions of water. It was then warmed and rapidly stirred with 4 liters of water for 15 minutes. This treatment, according to Hahn, will dissolve from the surface any adsorbed ions. The solution was cooled, and the supernatant liquid decanted. This warming procedure was repeated three times. Then the precipitate was placed in the washing tower shown in figure 1 and agitated as some 60 liters of water were slowly passed through the crystals from below. No test for nitrates was obtained when 20 cc. of the wash water was evaporated to dryness and the phenolsulfonic acid test was used. The washed crystals were then dried on a thoroughly cleaned porous tile and warmed to 60°C. to 110°C. in an electric oven. The crystal powder was stored in a crystallizing dish over phosphorus pentoxide in a desiccator.

Second method. The potassium bromide or iodide solution was first added to the water as above and the thallium nitrate solution was dropped in with rapid stirring. The precipitated powder was then put through the same steps as given above.

Third method. The thallium nitrate was first added to the water and the potassium bromide or iodide solution was dropped in with rapid stirring. The rest of the procedure was carried out as stated.

Thorium B nitrate solution

Thorium B was collected as described in the paper of King and Romer (1). After about sixty-four hours the loops were removed and the thorium B was dissolved in 5 cc. of warm 0.2 *N* nitric acid. This solution was then washed into a 100-cc. volumetric flask, 13 cc. of 0.2 *N* nitric acid added, and the whole made up to 100 cc. with water. One cc. of this solution was then removed, evaporated to dryness, and its activity determined in a beta ray electroscope. The volume was then adjusted with nitric acid of equal concentration so that 1 cc. of the resultant solution when evaporated to dryness had an activity of approximately 150 scale divisions per minute. This constituted the stock solution of thorium B nitrate.

Thallium nitrate stock solution

A thallium nitrate solution slightly more concentrated than 0.2 *N* was prepared. This was standardized gravimetrically by precipitating thallium iodide in 50 per cent alcoholic solution. The solution diluted to 0.2 normal was used as the stock solution of thallium nitrate.

Potassium bromide stock solution

A 0.2 normal potassium bromide solution was prepared by standardization with silver nitrate using potassium chromate as an indicator.

Potassium iodide stock solution

A 0.05 normal solution of potassium iodide was prepared by standardizing gravimetrically by precipitation of silver iodide (dark room).

Potassium chloride stock solution

A 0.05 normal solution of potassium chloride was prepared by titration against silver nitrate solution using potassium chromate as an indicator.

Potassium thiocyanate stock solution

A 0.05 normal solution of potassium thiocyanate was prepared by titration against test silver dissolved in nitric acid, using ferric alum as an indicator.

Potassium chromate stock solution

A 0.05 molar potassium chromate solution was prepared by treatment with sulfuric acid and potassium iodide and titration of the liberated iodine with standard sodium thiosulfate solution.

Chromic acid stock solution

A 0.05 molar chromic acid solution was made by dissolving chromium trioxide in water and titrating against sodium hydroxide with phenolphthalein as indicator.

Potassium phosphate stock solution

A 0.05 molar potassium phosphate solution was made according to the gravimetric method given in Griffin, Technical Methods of Analysis, page 764.

Phosphoric acid stock solution

The phosphoric acid solution was 0.05 molar and was standardized against sodium hydroxide using methyl orange and phenolphthalein as primary and secondary indicators.

Potassium oxalate stock solution

The 0.05 molar solution of potassium oxalate was prepared by standardization against potassium permanganate in acid solution.

Silver nitrate stock solution

The 0.2 normal solution of silver nitrate used was prepared by titration against standard potassium thiocyanate solution, using ferric alum as an indicator.

Lead nitrate stock solution

A 0.098 normal lead nitrate solution was standardized according to Olsen, Quantative Analysis, page 75.

Cupric nitrate stock solution

A 0.02 normal copper nitrate solution was prepared by standardization in the electrolytic deposition of the copper.

The watch glasses

The watch glasses used were matched in sets, each watch glass in a set having approximately the same diameter, curvature, and thickness. It is important in the activity measurements that the radioactive material be always in a thin layer of a salt deposited uniformly on these watch glasses and that this layer be always the same distance from the aluminum window of the electroscope. A varying distance from the aluminum window of the electroscope causes errors not only because of the different absorption in the air layer but also because of the scattering effect of the beta particles. A thin, even deposit of active salt is essential for duplication of measurements. This meant that the evaporation of the samples on the watch glasses had to be controlled. More soluble salts precipitated out more readily than less soluble salts. The evaporation was carried out on a water bath heated by controlled electrical heaters. The water bath was level. The watch glasses containing the active solutions were leveled and a regulated volume of air was blown over the surfaces by an electric fan. Special attention was given here to a series of evaporations so that the control experiment as well as the rest of those in the series had the same treatment in the evaporation procedure.

The bottles

The bottles used for shaking were about 40 cc. in volume and fitted the centrifuge cups so that no transfer of solution was necessary.

The pipettes used were either standardized by the Bureau of Standards or standardized by weighing their content of water.

The cleaning of glassware

All glassware in the work was allowed to stand for one hundred hours or more after using so that there was very slight residual activity. The glassware was then allowed to stand in concentrated chromic acid and sulfuric acid to remove traces of impurities and grease. It was then rinsed with distilled water and the special water of low conductivity. Grease on the watch glasses caused the solutions to evaporate unevenly, giving activities which could not be reproduced. The bottles were steamed out between measurements.

The electroscope

The electroscope used was described in the work of King and Romer (1). It was calibrated and adjusted so that different parts of the scale were equal, but for most of the work the same part of the scale was used so as to eliminate errors due to change in calibration. The procedure of King and Romer (1) was employed in all the activity measurements.

METHOD OF PROCEDURE

The carefully dried powder was weighed out into each bottle. Different volumes of water and of the solutions of the ions being studied were added, making the total volume of solution 25 cc. To this was added 5 cc. of a nitric acid solution of thorium B. The amount of nitric acid in the thorium B solution was such that the total volume of 30 cc. was always 0.006 normal in nitric acid. The bottles were then closed with glass stoppers, placed in a shaking machine, and shaken for one hour. The bottles were next placed in the centrifuge and centrifuged for 15 minutes at 1500 r.p.m. Without disturbing the precipitate, a dry 5-cc. pipette was rinsed out with the clear solution. Then two 5-cc. portions of the solution were pipetted out on watch glasses and dried by evaporation in a stream of air. The dried precipitate on the watch glass was then allowed to stand for eight hours or until radioactive equilibrium had been reached. For each series of solutions a measurement was made on a "control." Bottles containing 30 cc. of the solution as made up above without the powder were handled identically and the activity of 5-cc. portions measured. All activities were calculated to T_0 for comparison.

EXPERIMENTAL RESULTS

1. The effect of bromide ion on the adsorption of thorium B by thallium bromide

Five-tenths of a gram of thallium bromide, prepared by the first method, were used as adsorbent. Two series were run. All measurements in series

I were calculated to T_0' and those of series II to T_0''. The results are given in table 1 and the data is plotted in figure 2.

2. *The effect of centrifuging*

A series of experiments was carried out to determine if there was any effect introduced into the work by the centrifuging step in the procedure.

TABLE 1

The effect of bromide ion on the adsorption of thorium B by thallium bromide

THALLIUM BROMIDE	POTASSIUM BROMIDE	ACTIVITY CORRECTED TO T_0	ADSORPTION
	Series I. 3 millimoles of nitric acid per liter		
gram	*millimoles per liter*	*scale divisions per minute*	*per cent*
0	0	44.8	
0.5	0	26.6	40.7
0.5	1.66	25.5	43.1
0.5	3.33	24.7	44.9
0.5	5.0	24.4	45.6
0.5	6.6	23.9	46.7
0.5	8.33	23.6	48
0.5	10.0	22.6	49.6
	Series II. Same concentration of nitric acid		
0	0	40.3	
0.5	0	23.9	40.7
0.5	1.66	23.1	42.7
0.5	3.33	22.3	44.7
0.5	5.0	22.0	45.5
0.5	6.66	21.6	46.4
0.5	8.33	21.3	47.2
0.5	10.0	20.9	48.2

Watch glass No. 1 of the second series when calculated to the same T_0 as watch glass No. 1 of the first series gave an activity of 44.6. The natural fall of the electroscope during these measurements was 0.7 scale division per minute, which has been taken into consideration in the "Corrected Activity."

Three-tenths of a gram of thallium iodide with 6.6 millimoles of potassium bromide per liter were used. All experiments were run in triplicate. The first set was run for 15 minutes at 1500 r.p.m. and there was found to be a 30.1 per cent adsorption. The second set was run for 30 minutes at 2500 r.p.m. and there was found to be an adsorption of 31.2 per cent.

3. *The effect of hydrogen-ion concentration on the adsorption of thorium B by thallium iodide*

The results of this study are given in table 2 and plotted in the curve given in figure 3. The results seem to indicate that an acid concentration

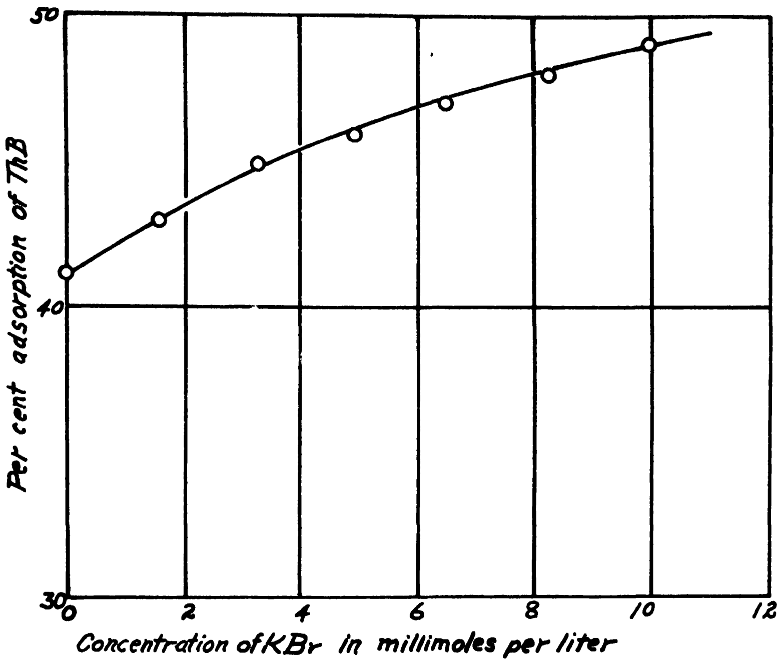

FIG. 2. ADSORPTION OF THORIUM B ON THALLIUM BROMIDE IN THE PRESENCE OF EXCESS BROMIDE IONS

TABLE 2

Effect of hydrogen-ion concentration on the adsorption of thorium B by thallium iodide

0.3 g. of thallium iodide used in all measurements. Each measurement was made in duplicate and the average for the two measurements is given.

NITRIC ACID	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
1 6*	62 4	
1 6	31 6	49.4
2 0	32 1	48.6
2.33	33 4	46.5
2 66	33 4	46.5
3 00	34 2	45.2
3.33	34 5	44.8
3.66	35.2	43.6
6.0	35 3	41.1
7.0	35.5	40.8
8.0	36 4	39.3
9.0	36 2	39.6
10 0	36 3	39.4

* Control; no thallium iodide.

of 6 millimoles per liter is sufficient to eliminate the main part of the effects due to adsorption on the glass walls or due to the formation of the colloidal particles of the thorium B.

4. *The effect of excess iodide ion and excess thallium ion on the adsorption of thorium B by thallium iodide*

In this series of experiments 0.3 gram of thallium iodide was used and the nitric acid concentration of the solutions was 6 millimoles per liter. The results are given in table 3 and the data is plotted in the curve given in figure 4.

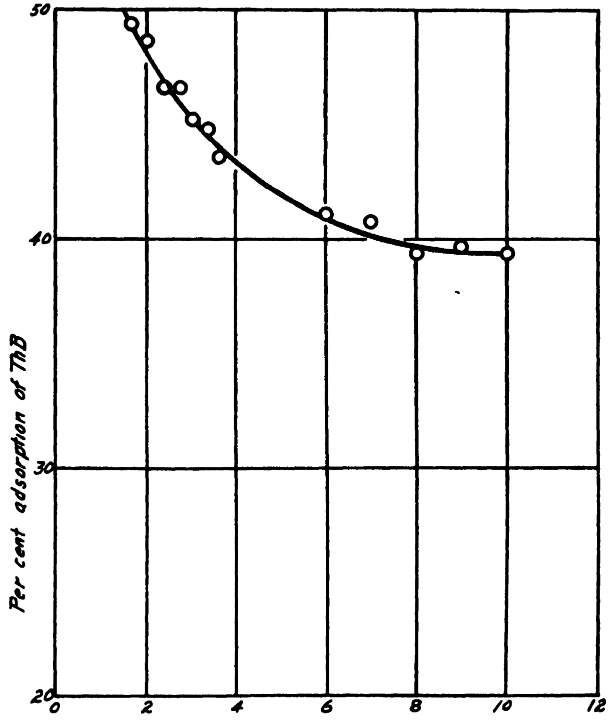

FIG. 3. ADSORPTION OF THORIUM B ON THALLIUM IODIDE WITH CHANGING HYDROGEN-ION CONCENTRATION

5. *Effect of an increase of the surface of the adsorbent on the amount of thorium B adsorbed*

In a duplicate series of runs 0.5 g. of thallium iodide in the presence of varying concentrations of excess potassium iodide was used. This data obtained is compared in curve I of figure 5 with that obtained in table 4 as given in curve II. It is to be realized that where the activity of a solution is removed to such an extent by the adsorbent as was the case in the great-

TABLE 3

Effect of excess iodide ion and excess thallium ion

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM IODIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	58.5	
0	39.4	32.7
0.55	19.7	66.4
1.1	10.2	82.6
1.66	7.1	87.9
3.33	3.9	92.2
8.3	1.4	97.6

THALLIUM NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	45	
0.66	37.5	16.6
1.34	40.1	10.9
2.00	41.4	8.0
2.66	42.2	6.3

* Control; no thallium iodide

TABLE 4

Effect of excess bromide ion

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM BROMIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	53.1	
0*	53.0	
0.833	34.9	34.3
0.833	34.5	35.1
1.66	34.9	34.3
3.33	35.0	34.1
3.33	34.4	35.2
5.00	34.4	35.2

* No thallium iodide.

est adsorption with 0.5 g. of thallium iodide the measurements on the residual activity of the solutions are of no great accuracy. The last point of curve I represents a measured activity (corrected) of 1.5 scale divisions per minute when the natural fall of the electroscope was 0.8 scale divisions per minute. In all the work in this paper, at least two samples of each solution were taken for analysis. Therefore to obtain the figure for an

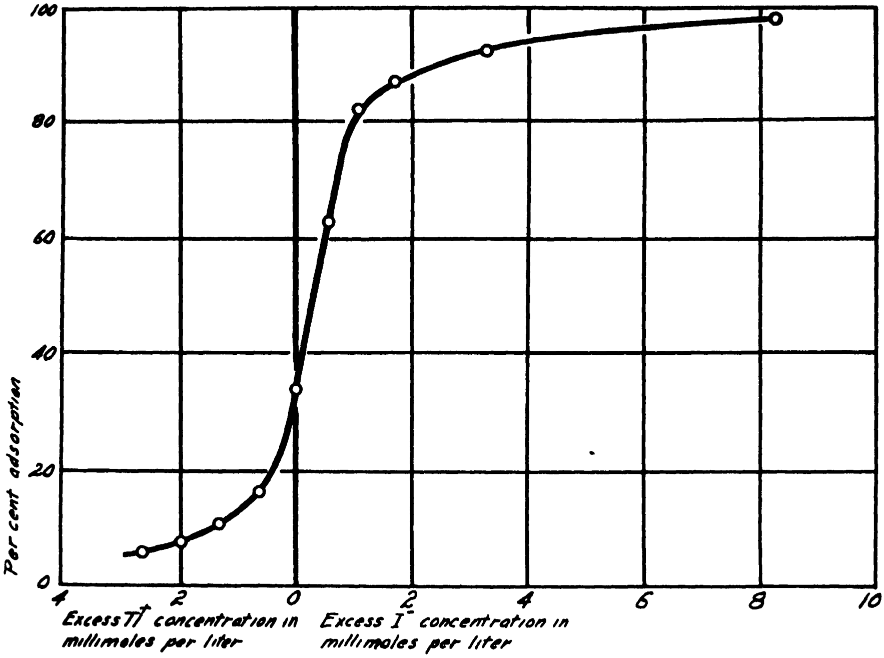

FIG. 4 ADSORPTION OF THORIUM B ON THALLIUM IODIDE WITH EXCESS THALLIUM IONS AND IODIDE IONS

TABLE 5

Effect of chloride ion on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0 3 g. of thallium iodide

POTASSIUM CHLORIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	49 9	
0 833	34 6	30 7
0 833	34 5	30 9
1 66	34 8	30 4
1 66	35 0	29 8
3 33	35 4	29 1
3 33	35 5	28 9
5 0	35 7	28 5
5 0	36 0	27 9

* Control; no thallium iodide.

average adsorption of 97.8 per cent (the last point on the curve), four measurements were made on two different solutions with two different samples of 0.5 g. of thallium iodide.

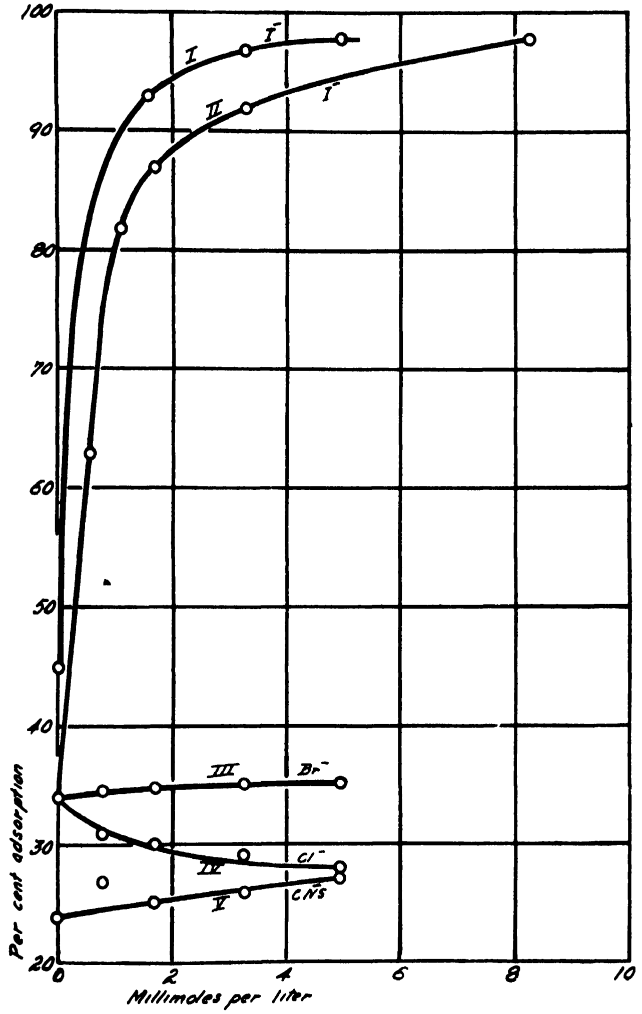

FIG. 5. ADSORPTION OF THORIUM B ON THALLIUM IODIDE IN THE PRESENCE OF VARIOUS ANIONS

6. Effect of bromide ion on the adsorption

Using a thallium iodide crystal powder which had an adsorption of 33.8 per cent, excess bromide ion was added. The results of this experiment are given in table 4 and plotted in figure 5.

7. *Effect of chloride ion on the adsorption*

In table 5 are given the results using chloride ion in place of bromide ion. The "neutral powder" used had an adsorption of 33.8 per cent. The data are plotted in the curve in figure 5.

TABLE 6

Effect of thiocyanate ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM THIOCYANATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	70.9	
0*	70.9	
0.833	51.9	26.8
0.833	49.4	30.3†
1.66	53.1	25.0
1.66	50.0	29.4†
3.33	52.3	26.2
3.33	52.3	26.2
5.00	51.5	27.3
5.00	51.6	27.4

* Control; no thallium iodide

† These results were discarded because of difficulties encountered in the evaporation of the active solutions on the watch glasses Owing to some cause the residue salts were unevenly distributed over the watch glasses

TABLE 7

Effect of chromate ions from potassium chromate on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM CHROMATE	pH OF SOLUTION	CORRECTED ACTIVITY	ADSORPTION	
millimoles per liter		*scale divisions per minute*	*per cent*	
0*	2.04	36.0		
0.83	2.31	23.0	36.2	
0.83	2.31	22.1	38.6	37.4
1.67	3.80	13.1	63.6	
1.67	3.80	15.9	55.9	59.9
3.33	5.23	4.3	88.0	
3.33	5.23	3.3	90.8	89.4
5.0	—	2.2	93.9	
5.0	—	1.8	95.0	94.5

* Control; no thallium iodide.

8. *Effect of thiocyanate ion on the adsorption*

The results of the measurements made using excess of thiocyanate ion are given in table 6 and plotted in figure 5. The crystal powder used in this series of measurements had an adsorption of 24.2 per cent.

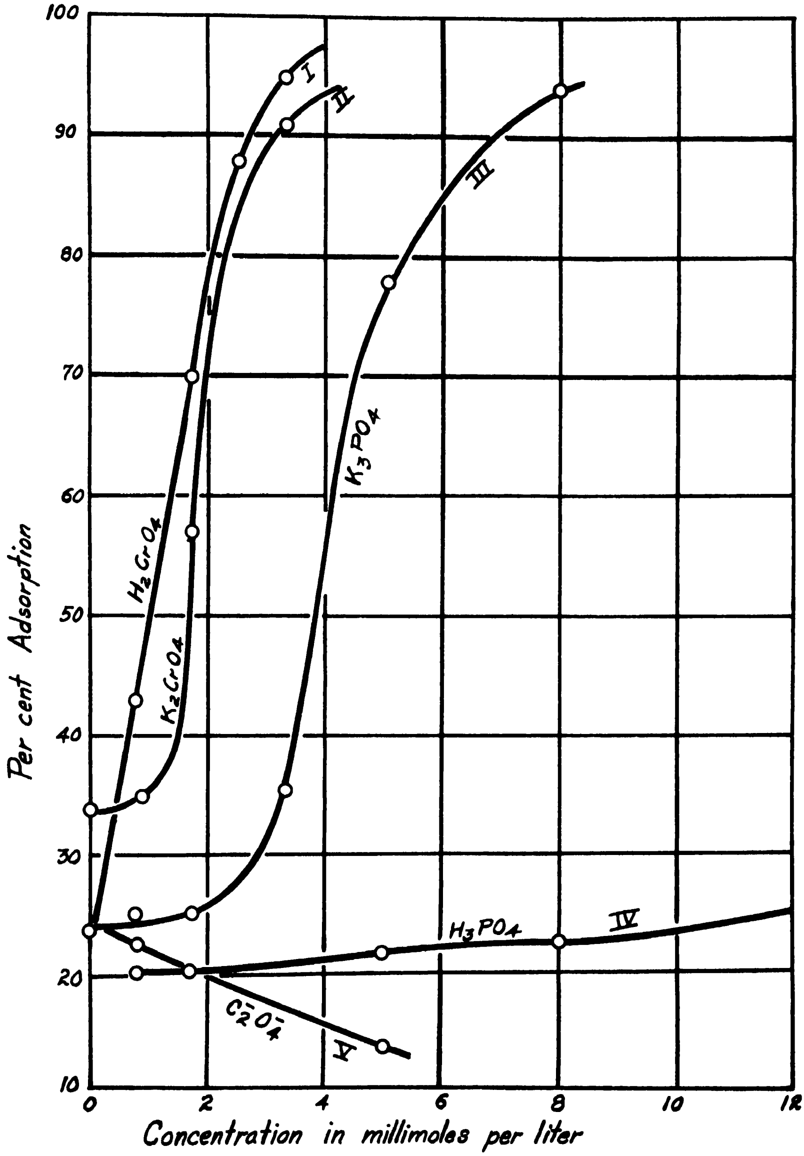

FIG. 6. ADSORPTION OF THORIUM B ON THALLIUM IODIDE IN THE PRESENCE OF VARIOUS IONS

9. *Effect of chromate ions on the adsorption*

The same experiments were carried out using excess chromate ions. In the first series of measurements, potassium chromate was used as a source of CrO_4^{--} ions. Since this introduced the complication of the hydrolysis of the potassium chromate with the resulting neutralization of the 6 millimoles

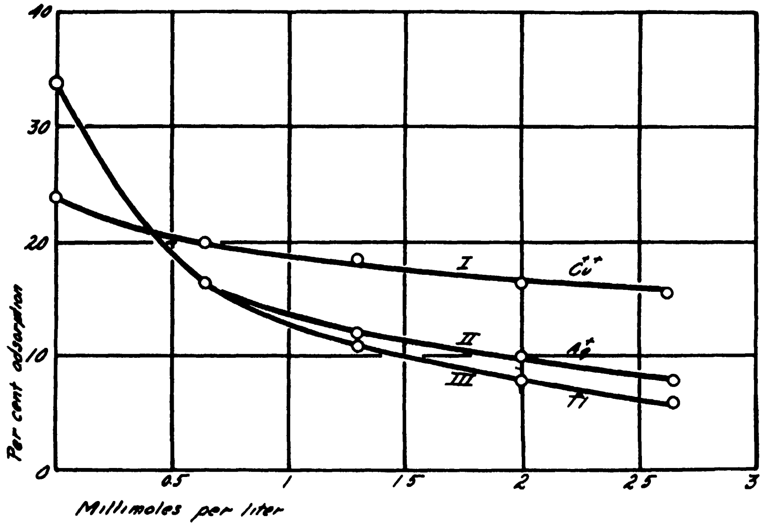

FIG. 7. ADSORPTION OF THORIUM B ON THALLIUM IODIDE IN THE PRESENCE OF EXCESS OF VARIOUS CATIONS

TABLE 8

Effect of chromate ions from chromic acid on the adsorption

Enough nitric acid was added to bring the H^+ ion concentration up to that recorded in the pH column

Adsorbent = 0 3 g of thallium iodide

CHROMIC ACID	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*		67 4	
0*		67 6	
0	2 6	54 5	19 4
0	2 6	55 4	19 3
0 833	2 6	38 2	43 5
1 66	2 6	20 4	69 9
1 66	2 6	20 0	70 5
2 5	2 7	8 7	87 2
2 5	2 7	8 1	88 1
3 33	2 7	3 3	95 2
3 33	2 7	3 3	95 2

Control; no thallium iodide.

per liter of nitric acid which was necessary in the solution to obtain reproducible results, another series of experiments was run using chromic acid as a source of chromate ions. An attempt was made to reduce the amount

TABLE 9

Effect of phosphate ions from potassium phosphate on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0 3 g of thallium iodide which had an adsorption of 24 2 per cent

POTASSIUM PHOSPHATE	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*	2 04	30 1	
0 83	2 24	22 6	25 0
1 67	2 38	22 8	24 3
1 67	2 38	22 6	25 0
3 33	5 39	19 3	36 0
3 33	5 39	19 6	35 0
5 0	7 10	6 5	78 4
5 0	7 10	7 0	76 8
8 0		3 0	94 0

* Control, no thallium iodide

TABLE 10

Effect of phosphate ions from phosphoric acid on the adsorption

Enough nitric acid was used to make the total H^+ ion concentration equal to that indicated in the column of pH measurements

Adsorbent = 0 3 g of thallium iodide

PHOSPHORIC ACID	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*		67 4	
0*		67 6	
0 83	2 29	54 2	19 9
1 67	2 36	53 7	20 6
1 67	2 36	54 5	19 4
5 0	2 28	53 0	21 6
5 0	2 28	52 8	21 9
8 0	2 29	52 0	23 1
8 0	2 29	52 5	22 4
16 7	2 22	45 9	32 2
16 7	2 22	47 3	30 4
16 7†	-	65 4	3 0
16 7†		65 0	3 6

* Control; no thallium iodide

† No thallium iodide

From the last two measurements there is an average "holding back" effect, due to the phosphoric acid, of some 3 3 per cent. This would make the corrected adsorption for the 10th and 11th measurements 28 0 per cent of nitric acid in the solution as the amount of chromic acid increased in order to keep the hydrogen-ion concentration constant. pH measurements were made on the solutions after the adsorption equilibrium had been reached, using the quinhydrone electrode. In the case of chromic acid it

TABLE 11

Effect of oxalate ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide which had an adsorption of 24.2 per cent

POTASSIUM OXALATE	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*	2.04	32.9	
0.83	2.13	25.4	22.8
0.83	2.13	25.8	21.6
1.67	2.16	26.2	20.3
1.67	2.16	26.3	20.3
5.0	2.46	28.7	12.8
5.0	2.46	28.2	14.2

* Control; no thallium iodide

TABLE 12

Effect of silver ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide with an adsorption of 33.8 per cent

SILVER NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	76.3	
0.66	64.1	16.0
0.66	63.1	17.3
1.34	67.0	12.2
1.34	67.7	11.3
2.00	69.2	9.3
2.00	68.0	10.9
2.66	69.5	8.9
2.66	70.3	7.9

* Control; no thallium iodide.

was difficult to obtain consistent results with this electrode because of the oxidizing action of the chromic acid. However, by using the voltage recorded at the beginning, fairly consistent results were obtained, which indicated that the acid concentration was sufficiently constant. The results are given in tables 7 and 8 and the data is plotted in the curves in figure 6.

10. Effect of phosphate ion on the adsorption

Because of the hydrolysis of the potassium phosphate used, with the resultant neutralization of the nitric acid in the solution, a second series was run using phosphoric acid as the source of the PO_4^{---} ion. In tables 9 and 10 are given the results of the experiments with excess phosphate ions and the pH measurements of the solutions. The results are plotted in figure 6.

TABLE 13

Effect of cupric ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide with an adsorption of 24.2 per cent

CUPRIC NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	73.9	
0.67	59.5	19.4
0.67	58.5	20.8
1.33	60.4	18.5
2.0	61.6	16.6
2.67	62.7	15.2
2.67	61.6	16.6

* Control; no thallium iodide

TABLE 14

Effect of lead ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide with an adsorption of 33.8 per cent

LEAD NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles × 10^{-3} per liter	*scale divisions per minute*	*per cent*
0*	46.2	
0.163	31.0	32.9
0.163	31.2	32.5
1.63	32.1	30.6
16.3	40.8	11.7
16.3	41.3	10.7
32.6	42.3	8.5
32.6	43.0	7.0

* Control; no thallium iodide.

11. Effect of the oxalate ion on the adsorption

In table 11 are given the results of the experiments in which an excess of oxalate ion was used. These results are plotted in the curve in figure 6.

12. Effect of silver ion on the adsorption

In table 12 are given the results of the measurements of the adsorption in the presence of excess of silver ions. The results are plotted in the curve in figure 7.

13. The effect of cupric ions on the adsorption

In table 13 are given the results of the experiments carried out on the adsorption in the presence of excess cupric ions. These results are shown graphically in the curve in figure 7.

14. The effect of the lead ions on the adsorption

In table 14 are given the results of the measurements in which the adsorption was allowed to take place in the presence of small concentrations of lead ions.

DISCUSSION OF RESULTS

1. It is to be noted that in no case have we been able to prepare a "neutral powder" which had no adsorption for thorium B ions (5). In all the experiments the concentration of the thorium B was kept constant as described on page 854 because work of King and Greene (6) will show that there is a slight difference in the amount of activity adsorbed from solutions of varying activity. In experiment 1 with thallium bromide as the adsorbent, as much as 10 millimoles per liter of potassium bromide caused an increase in the adsorption of only some 8 per cent. We found that with this amount of excess potassium bromide there was no measurable "holding back" effect. This small increase in adsorption can be explained by the relatively high solubility of the thallium bromide, 1.7 millimoles per liter.

2. Experiment 2 shows that centrifuging the samples at 1500 r.p.m. for ½ hour is sufficient to remove any fine particles of powder from the solution which might have adsorbed thorium B ions and caused an apparent larger activity of the supernatant solution used for analysis.

3. Experiment 3 is concerned with one of the most interesting phases of the whole problem, namely, the question of the physical condition of the radioactive material in the solution, which has been discussed in the paper by King and Romer (1). In addition to the possibilities of "pseudo colloids," "radiocolloids," hydrolyzed particles of thorium B and thorium C and the charge on the walls of the glass vessels, all of which are affected by the amount of hydrogen ion, there is also the possibility of the competition of hydrogen ion with thorium B ions for a place on the surface of the crystals. This was brought out in the paper of Fajans and Erdey-Grúz who found that there was a large decrease in the amount of thorium B adsorbed on several silver salts when the acid concentration of the acid in the solution increased from 0.004 normal to 0.05 normal.

4. Experiment 4 shows the effect of increasing the minus charge on the thallium iodide crystals by the addition of iodide ions and that of decreasing the minus charge by the addition of thallium ions. The adsorption phenomenon is continuous, as shown by the curve in figure 4. With an excess of 2.7 millimoles of thallium nitrate per liter, there is still an adsorption of some 6 per cent. This does not necessarily mean that the thallium iodide crystals are still negatively charged. Lange and Crane (2) found silver iodide crystals neutral at a silver ion concentration of 1×10^{-5}. Fajans has shown by electroendosmosis experiments that thorium B ions can be adsorbed on silver salt particles which are positively charged.

5. In experiment 5 no direct determination was made of the magnitude of the surface of the thallium halide crystals used. From repeated tests the surface per gram remained constant for the purposes of our experiments. The same preparation of thallium halide salt was used for each series of measurements. Experiment 5 shows the increase in the adsorption caused by an increase in surface of that of 0.3 g. to that of 0.5 g. J. Walker estimated the surface of his silver bromide by microscopic method to be 2×10^3 sq. cm. per gram.

6. Experiments 6, 7, and 8. From observation of figure 8 it can be seen that the effect of the anions on the adsorption is in the order

$$I^- > CNS^- > Br^- > Cl^-$$

It is to be noted that not all measurements were made on the same sample of powder.

The differences in the amounts of adsorption of thorium B by two different preparations of "neutral powder" can be attributed to the differences in the surface per gram of the different powders and also the difference in the numbers of points on the crystals to which are attached halide ion (i.e., the charge on the particles). The change in the adsorption due to the addition of an electrolyte represents the ability of the electrolyte to increase the charge on the crystal, that is, to add a further excess of anions to the crystal. Therefore we are able to compare the effect of two different anions on two different preparations of powders. For instance, 3.3 millimoles per liter of excess potassium bromide on one powder caused an increase in the adsorption of thorium B of 0.9 per cent, while the same amount of excess potassium thiocyanate on another preparation caused an increase in the adsorption of 2 per cent.

If results obtained using an excess of the salt of 3.3 millimoles per liter are taken for comparison, we find for

I^-	an increase of 58 per cent in adsorption
CNS^-	an increase of 2 per cent in adsorption
Br^-	an increase of 0.9 per cent in adsorption
Cl^-	a decrease of 5 per cent in adsorption

Fajans found this same order for the ions in his study of the displacement of erythrosinate ion from the surface of silver iodide. From the solubility table given on page 873 it is seen that thallium thiocyanate is more soluble than thallium bromide. In other words, the thiocyanate ion is out of order on a strict solubility consideration because thiocyanate ions are better adsorbed than are bromide ions. Fajans showed the same to be true in the case of the adsorption of thorium C on silver sulfide. The adsorption rule which states that adsorbability is related to insolubility is to be applied to similar or analogous ions. The order of adsorbability and insolubility holds good for the halide ions. In the case of the large organic dye ions—eosinate and erythrosinate—the rule also holds. Silver eosinate has a solubility of 5×10^{-5} moles per liter, while silver erythrosinate has a solubility of 1.1×10^{-6}; that is, silver eosinate is about fifty times as soluble as silver erythrosinate. On 1 g. of silver bromide in a solution 2×10^{-6} molar in erythrosinate ion, 15 per cent of the erythrosinate ions were adsorbed, but when 1 g. of silver bromide was brought to equilibrium in a solution of eosinate ion five times more concentrated only 5 per cent of the eosinate ions were adsorbed. When halide ions are compared with large organic dye ions, another determining factor enters. The halide ions were used to replace adsorbed erythrosinate ions from the surface of silver halides. It was shown that even though silver erythrosinate was more soluble than the silver halides, the erythrosinate ion was much more adsorbed. Therefore, in addition to the simple electrostatic attraction which exists between a large ion and the crystal surface, another factor due to the non-polar forces or semipolar forces (deformation effect) becomes significant. For this reason it can be expected that the large dissimilar thiocyanate ion is more readily adsorbed than the bromide ion even though thallium bromide is more insoluble than thallium thiocyanate.

7. An effect in experiments 7 and 11 (shown in the curves in figures 5 and 6) is to be noted. Here an excess of potassium chloride and potassium oxalate decreases the amount of adsorption. Addition of 5 millimoles of potassium chloride per liter causes some 6 per cent decrease, and addition of the same amount of potassium oxalate causes a decrease of some 11 per cent. Thallium chloride is soluble to the extent of 13 millimoles per liter, and thallium oxalate to the extent of 53 millimoles per liter. This high solubility should be accompanied by a slight tendency for chloride ion and oxalate ion to be adsorbed. Since all ions possess some tendency to become attached to the surface of a crystal lattice, we have here in this case an opportunity for potassium ions to be adsorbed along with thorium B ions (or potassium ions to decrease the charge on the crystal and thereby decrease the amount of thorium B adsorbed). In other words, a large concentration of potassium ions may replace from the surface some thorium B ions as did the hydrogen ions as discussed above. When Fajans used

potassium chloride to replace the erythrosinate ions from the surface of silver iodide, he found an increase of adsorption rather than a decrease. Further work on the adsorption of the alkali ions and the alkaline earth ions is to be reported in a subsequent paper.

8. Experiments 9 and 10 deal with work on adsorption in the presence of an excess of a hydrolyzable electrolyte. In curve III in figure 6 the apparent adsorption is mainly due to the neutralization of the nitric acid by the potassium hydroxide formed in the hydrolysis and the subsequent adsorption of a kind discussed in paragraph 3 (p. 870). In curve IV of the same figure the adsorption is due to the addition of an ion which does not form a very insoluble compound. In figure 6 where hydrolysis takes place and also the anion forms an insoluble compound, curve I shows the increasing of the charge on the particles by the chromate ions and curve II shows an increasing of the charge and a neutralization of the acid.

TABLE 15

ION	PER CENT INCREASE IN ADSORPTION	SOLUBILITY
		millimoles per liter
I^-	58	0.18
*CrO_4^{--}	51	0.57
CNS^-	2	12.0
Br	1.9	1.7
*PO_4^{---}	0.0	7.0
Cl^-	−5.0	13.0
*$C_2O_4^{--}$ *	−4.0+ but decreasing more rapidly than Cl^-	53.0

* Milliequivalents per liter

9. In table 15 the ions are listed in the order of their adsorbability on thallium iodide; also the per cent increase in the adsorption for 3.3 millimoles per liter of the electrolyte and the solubilities of the thallium salts are given. The order of adsorbability runs parallel with that of insolubility if the exception discussed above is made for thiocyanate ion.

10. In experiments 12, 13, and 14 it is shown that a cation which forms an insoluble salt with the anion of the crystal is adsorbed and will replace thorium B ions from the surface. In figure 7 are plotted the results for copper, silver, and thallium ions. Because copper iodide is more soluble than silver iodide, the copper ions do not replace thorium B as well as silver ions do. Silver iodide is less soluble than thallium iodide, but thallium ions are better adsorbed than silver ions, because in this case the thallium ions fit better into the crystal lattice than do silver ions. Lead ions and thorium B ions are equally well adsorbed by the crystals.

SUMMARY

1 A report has been given of a series of experiments carried out to determine the effect of various anions and cations on the adsorption of thorium B ions on thallium bromide and thallium iodide crystals

2 The purest thallium bromide and thallium iodide which could be prepared showed a negative charge and adsorbed thorium B ions

3 The adsorption rule which postulates that the insolubility of the salt formed by the ion being adsorbed with the oppositely charged ion of the crystal determines the adsorbability of the ion has been verified for I^-, CrO_4^{-} , CNS , Br^-, PO_4^{-} $^-$, Cl^-, $C_2O_4^{--}$ ions on thallium iodide crystals

4 The ionic deformation theory has been used to explain the relative adsorbability of the halide ions and the thiocyanate ion

5 The question of the effect of hydrogen ion on the adsorption of thorium B on thallium iodide has been discussed

6 Results have been reported on the measurements made of the effect of Ag^+, Cu^{++}, Tl^+, and Pb^{++} on the adsorption of thorium B on thallium iodide crystals

REFERENCES

(1) King, J F , and Romer, A J Phys Chem **37,** 663 (1933) References to the literature

(2) Lange, E , and Crane, P W Z physik Chem **141,** 225 (1929)

(3) Reference 4, page 107

(4) Fajans, K , and Erdey-Grúz, T Z physik Chem **A158,** 117 (1931)

(5) Hahn, O , and Imre, L Z physik Chem **A144,** 168 (1929)

(6) To appear in a subsequent issue

THE ABSORPTION SPECTRA OF A SERIES OF ORGANIC MOLECULAR COMPOUNDS[1]

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Pfeiffer (1) and others have investigated the colored molecular compounds resulting from quinones with aromatic hydrocarbons, ethers, or amines. Pfeiffer has classified these compounds with the quinhydrones and has shown that a series extends from the intensely colored quinhydrones existing as crystalline compounds, through colored complexes difficult to crystallize, to complexes impossible to crystallize and identified largely by a slight color change on mixing the liquid components. These latter "molecular compounds" are tied by forces which are weak in comparison with the intermolecular forces in the crystals of the components, for, on cooling, the components of the mixture crystallize out separately. Foreign solvents tend to dissociate the compounds and as a result Beer's law does not hold.

We undertook a spectroscopic study of the more weakly tied compounds of this type in the hope of extending the series of molecular compounds to loosely tied complexes which had escaped detection because the color change occurred in the ultra-violet or was too slight to be seen with the eye. There was also the possibility that the "solvent effect" of absorption spectroscopy could be linked with these color changes. Foremost, however, there was the hope that a correlation between color and oxidation-reduction potentials might be established.

RESULTS

We have carried out quantitative light absorption measurements on the five quinones—chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone—in a melted state and in the absence of any solvent. The resulting curves are compared with the light absorption of equimolecular mixtures of these quinones with various aromatic ethers, hydrocarbons, and amines. Thirty-three such combinations were investigated. No third component was used as solvent because of the probable dissociation it would involve; instead a thin layer of the liquid mixture was employed, necessitating the use of special absorption cells and technique. However, it is convenient to refer to the nonquinoid component of the equimolecular mixture as "solvent." This will be done in the subsequent discussion.

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[1] This article is based upon the thesis of E. H. Northey submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1930. The manuscript was prepared by the junior author after the death of Dr. Hunter in 1931.—L. I. Smith.

[2] du Pont Fellow in Chemistry, 1929–1930.

Practical considerations limited our choice of components. Melting points and vapor pressures of the pair had to be nearly equal, otherwise changes in composition occurred during measurement. Thus di-, tri- and tetra-chloroquinones were eliminated on account of their high melting points, and benzene, toluene, and hexamethylbenzene were eliminated on account of their high vapor pressures.

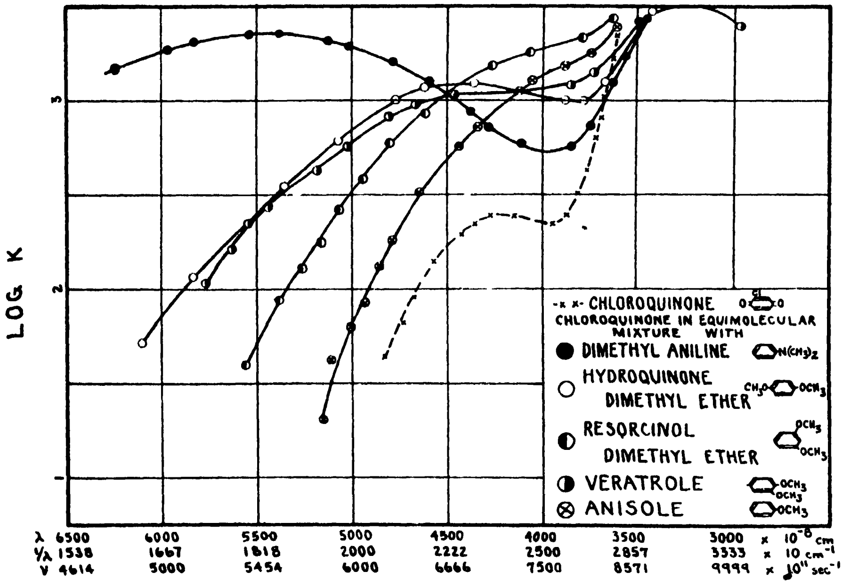

FIG. 1. CHLOROQUINONE

The results as shown in figures 1 to 7 are expressed in terms of the extinction coefficient as defined by the Bunsen-Roscoe law:

$$K = \frac{1}{d} \log_{10} \frac{I_0}{I}$$

where d is the thickness of absorbing layer in centimeters. These curves compare the absorption of a quinone with the absorption of its molecular compounds with various "solvents," assuming complete combination. Actually an equilibrium mixture was undoubtedly present and account

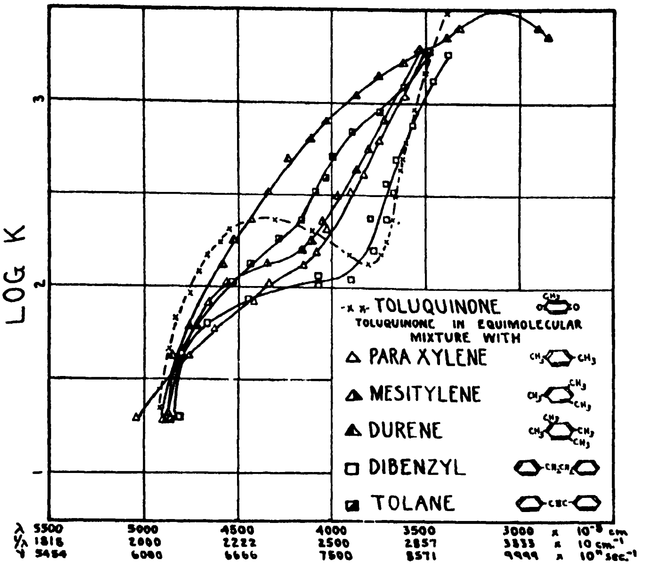

FIG. 2. CHLOROQUINONE

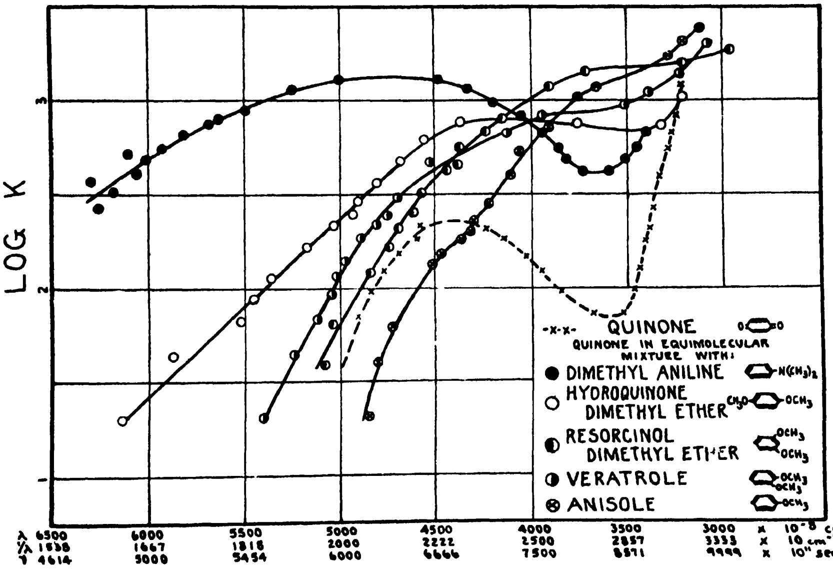

FIG. 3. QUINONE

should be taken of the absorption of uncombined quinone,[3] but since the dissociation constants were lacking, no correction could be made. However,

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[3] The solvents are nearly transparent in the region studied and their slight absorption was corrected for during measurement.

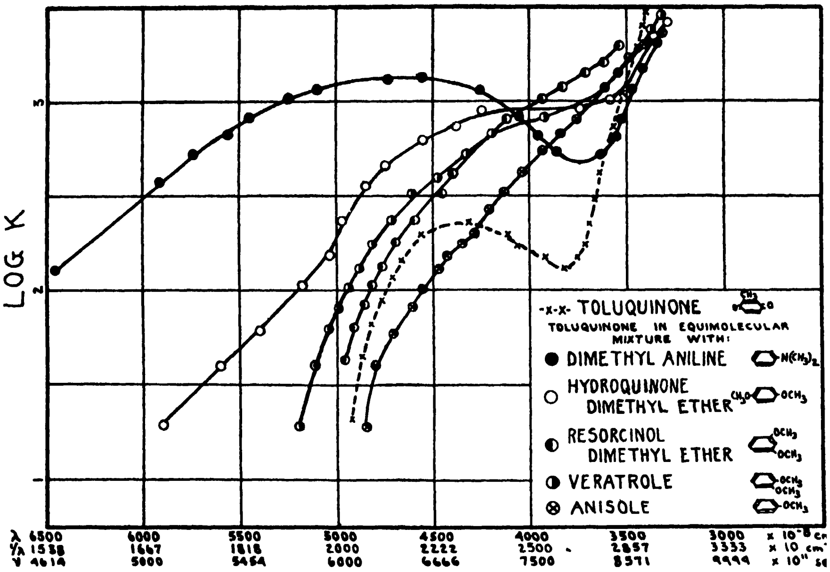

FIG. 4. TOLUQUINONE

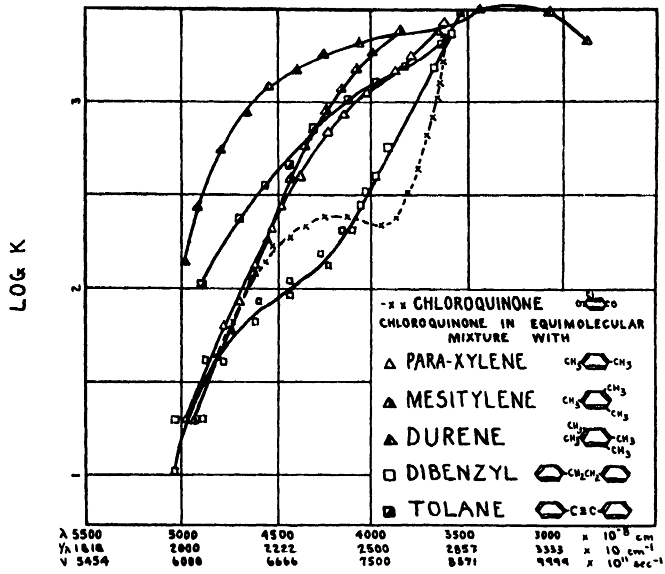

FIG. 5. TOLUQUINONE

it was of considerable interest to replot the data on the assumption of no compound formation, i.e., it was assumed that the only effect of the "solvent" was simple dilution, and by calculating back to the absorption of quinone with solvent removed, curves were obtained which show the "sol-

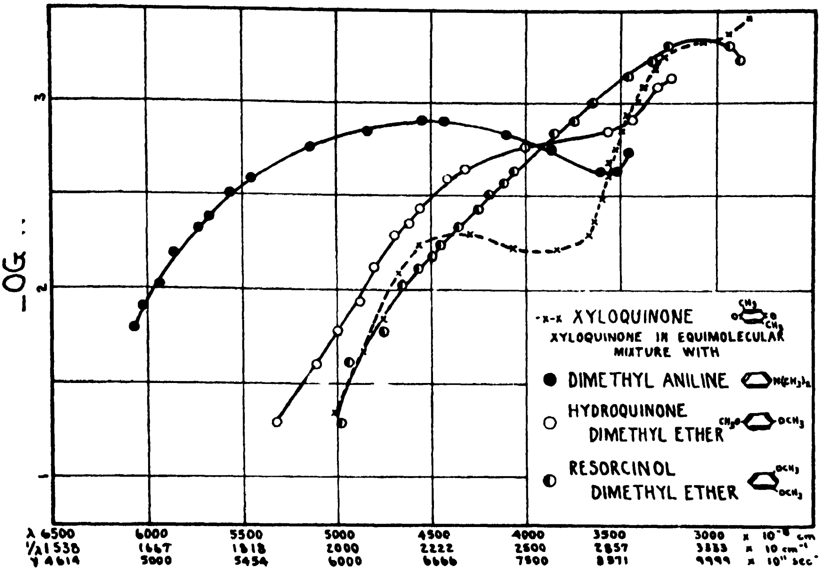

FIG. 6. XYLOQUINONE

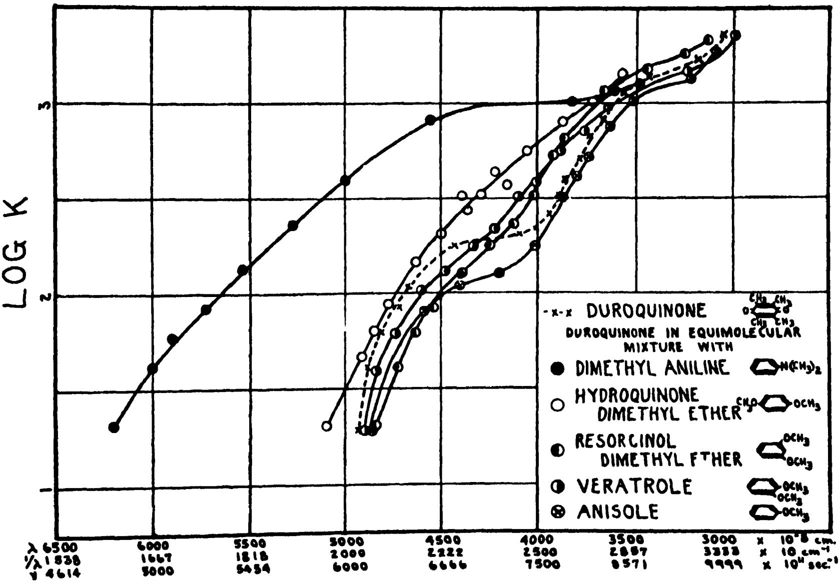

FIG. 7. DUROQUINONE

vent effect" to better advantage. Calculated in this way, and granting the assumptions, the absorption curves of a pure quinone and its various "solutions" should be identical.

Let K = the measured extinction coefficient of a quinone in solution, and K' = the extinction coefficient with solvent removed. K′ will differ from K only in the thickness of the absorbing layer if the solvent is transparent and otherwise inert. The relationship is:

$$K' = \left[1 + r\frac{M_s S_q}{M_q S_s}\right] K$$

or

$$\log K' = \log K + C$$

where

$$C = \log\left[1 + r\frac{M_s S_q}{M_q S_s}\right]$$

TABLE 1

Values of C for equimolecular mixtures of quinone and "solvent"

	CHLORO-QUINONE	QUINONE	TOLU-QUINONE	DURO-QUINONE
Dimethylaniline.	0 35	0 41	0 33	0 25
Hydroquinone dimethyl ether	0 36	0 42	0 34	0 26
Resorcinol dimethyl ether	0 36	0 42	0 34	0 26
Veratrole	0 35	0 41	0 33	0 25
Anisole	0 31	0 36	0 29	0 22
p-Xylene.	0 34		0 32	
Mesitylene	0 37		0 35	
Durene	0 40		0 38	
Dibenzyl	0 38		0 36	

and M_s = molecular weight of "solvent,"
M_q = molecular weight of quinone,
S_s = density of "solvent,"
S_q = density of "quinone," and
r = mole ratio of "solvent" to "quinone."

Hence if log K is replotted as log K' the curve will simply be raised by an amount equal to C.

Densities of "solvent" and quinone must be known slightly above the melting point to make use of the formula. Most of the data needed were found in the literature, but rough determinations had to be made on the quinones. These densities are: for chloroquinone, $d^{60°}$ 1.38; toluquinone, $d^{70°}$ 1.07; duroquinone, $d^{115°}$ 1.02. A value for quinone was found in the literature, while insufficient xyloquinone was available for a determination.

The calculated values of C are given in table 1.

DISCUSSION OF RESULTS

Figure 8 shows the data on duroquinone replotted in terms of log K'. It is apparent that there is an effect of "solvent" other than simple dilution, since the "solution" curves deviate from that of the pure quinone. In the case of anisole this deviation is relatively small and is comparable with changes in the absorption spectrum of any substance observed by changing from one solvent to another. The increased effect of veratrole is still of the order of solvent effects and would be so ascribed in the absence of other data. There can be little doubt, however, that if the solvent effect is met with in the case of duroquinone it is the result of the same influences causing color changes in the case of chloroquinone. Since Pfeiffer has demonstrated that these color changes are a part of molecular compound formation, it appears that we have bridged the gap between true molecular compounds and one type of solvent effect.

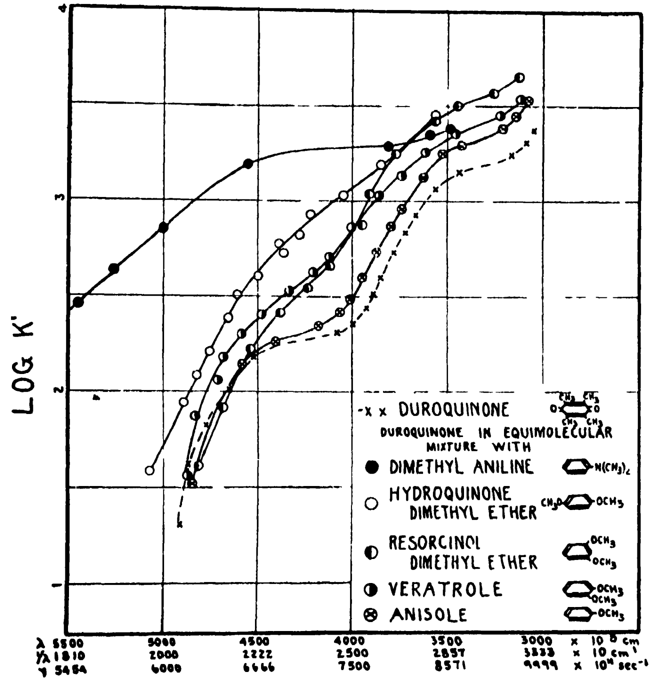

FIG. 8. DUROQUINONE

Comparison of figures 1 to 7 for any one "solvent" shows that the difference between the "solution" curve and quinone curve increases in the order duroquinone, xyloquinone, toluquinone, quinone, chloroquinone. In order to put these differences on a numerical basis we have arbitrarily measured the areas between the quinone curve, $\log K = 1.5$, and the "solution" curves. The unit of area has no significance and the choice of $\log K$ at 1.5 was for convenience, as such choice does not affect the order of the results.

In figure 9 we have plotted these areas against Conant and Fieser's (2) values of π_s, the reduction potential in volts, of the respective quinones. Two generalizations can be drawn from these data:

I. In a series of quinones the change in the absorption spectrum, brought about by a solvent capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.

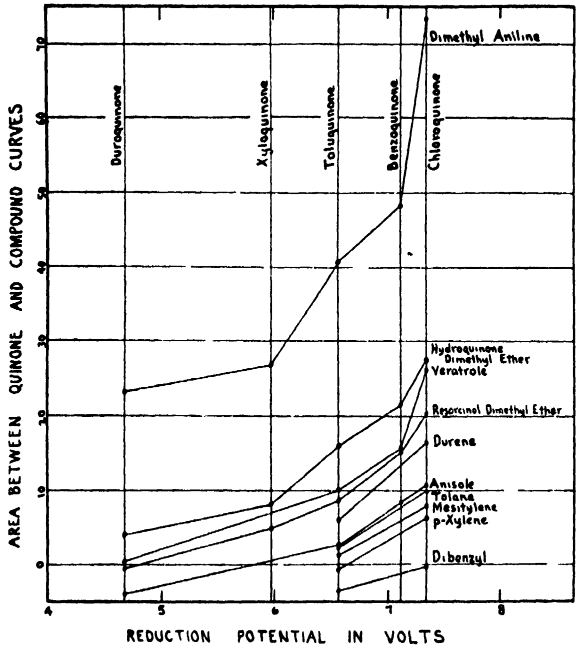

Fig. 9

II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

The significance of these findings with respect to color theories is evident; however, additional experimental work along several lines is necessary in order to place the results here obtained in their proper relation. Since no further work is possible in the near future, the results are published in the hope that they may be of use elsewhere.

EXPERIMENTAL

Apparatus

All measurements of light absorption were carried out quantitatively by means of a Judd Lewis sector photometer (Hilger H-41) and Hilger E-2 spectrograph. The light source was an under-water tungsten spark (3). Spectra were photographed on Wratten and Wainwright panchromatic plates. Points of equal density on paired spectra were found by use of a Moll type A microphotometer especially adapted to the work by adding a longer galvanometer scale, a more powerful light source, and an elevating lever for rapid shift from one spectrum to the other. Match points were marked on the emulsion by a fine scratch and their wave lengths were later read off from calibrated wave length scales photographed on the plate.

Instead of diluting with a solvent to obtain high values of the extinction coefficient we had to use extremely thin layers of the melted compounds. Absorption cells as shown in figure 10 were therefore constructed. Fused quartz plates 2 x 2 cm. square x 3.5 mm. thick, ground optically flat to a tolerance of 0.001 mm. were spaced apart by thin strips of pure gold, 2 mm. wide by 2 cm. long, which were laid along two sides and the bottom. The thickness of the gold varied from 0.075 to 0.005 mm. depending on the range of log K required, the thinnest layer permitting a value for log K of 3.5 to be measured. All metal parts of the cell were heavily gold plated to resist corrosion by the quinones.

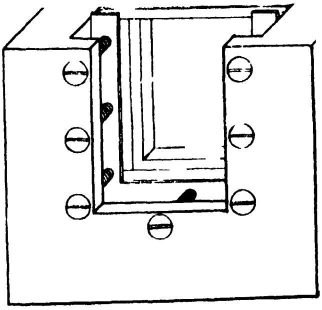

FIG. 10

As it was necessary to keep the mixture molten while spectra were being taken, a cell heater was constructed to set on the table of the photometer in place of the usual cell supports. This was of sheet iron construction inside and out, insulated electrically with mica and thermally with magnesia. Windows of 2-cm. brass tubing provided passage for the two light beams of the photometer. The two windows at the end nearest the spectrograph were closed on the inside with thin quartz discs to prevent vapors from condensing on the collimating lenses of the photometer. The other windows were left open to prevent the accumulation inside the heater of sufficient vapor to affect the results. Heat was applied electrically by resistance wire wound around the core and regulated with a lamp bank to give a temperature about two degrees above the melting point of the substances studied.

Technique

In the assembly of the absorption cells, the quartz plates were first cleaned with extreme care. All subsequent handling was done with smooth-jawed brass forceps. After assembly, the cell thickness was made uniform by adjusting the seven small screws bearing against the U-shaped strip of brass. The cell was viewed by reflected light from a Pyrex mercury arc, and adjustment was varied until the interference bands which appeared were lined vertically with the cell and as few in number as possible. A minute variation in thickness across the cell was of slight concern, since in measuring both cell thickness and light absorption an average value was obtained; variation from top to bottom caused a gradation in density across the spectrum, however, and was avoided.[4] The empty cell after adjusting as above, was held at the slit of a spectrograph and illuminated by a powerful continuous light source.[5] The spectrum of the empty cell was photographed and adjacent to it the mercury arc spectrum. The number of dark interference bands between two lines in the mercury arc was counted. The cell thickness was then found using the formula:

$$\frac{\frac{n}{2}}{\frac{1}{\lambda_1}-\frac{1}{\lambda_2}}$$

where d = thickness of cell, and

n = the number of dark bands between wave lengths λ_1 and λ_2.

Unless the cell was of uniform thickness from top to bottom, the interference bands were sloped and indistinct.

Two cells were placed in the heater. One contained the melted compound; the other, containing the "solvent," served to correct for light reflected from the faces of the first cell and for light absorbed by the "solvent." In taking the spectra of pure quinones this second cell was empty, the two quartz plates being spaced to avoid interference bands.

Equimolecular amounts of the quinone and "solvent" were weighed into a test tube made of an 18-cm. length of 8-mm. Pyrex tubing. A 20-cm. length of 3-mm. tubing drawn to a tip at one end made a sort of elongated medicine dropper for transferring the melted substance from test tube to absorption cell. The tip of the dropper was placed at the space between the quartz plates. Providing the cell had been properly cleaned, surface tension then filled the cell completely. The cell was always inspected to see that no air bubbles remained.

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[4] We are indebted to Professor Valasek of the Physics Department for suggesting the method of measuring cell thickness.

[5] Hilger E I spectrograph and 500-watt projection bulb.

Preparation and purification of materials

Dimethylaniline. The commercial product was treated with acetic anhydride, carefully fractionated under vacuum, and finally purified by three crystallizations from its own mother liquor. n_D^{20} 1.5570; given in the literature, 1.55873.

Hydroquinone dimethyl ether. Kahlbaum's product was twice fractionated *in vacuo.* Melting point 56°C.; given in the literature, 56°C.

Resorcinol dimethyl ether. Resorcinol was methylated with dimethyl sulfate and the crude product purified by steam distillation, vacuum distillation, treatment with metallic sodium, and again vacuum distillation. Boiling point, 82.5–84°C. at 5 mm.; given in the literature, 216.5–217.7°C. at 760 mm.

Veratrole. Guaiacol was methylated with dimethyl sulfate and the product twice vacuum distilled. The fraction boiling at 100–106°C. at 18 mm. was partially frozen and the crystals separated. This was repeated six times, the melting point rising to 22°C.; given in the literature, 23°C.

Anisole. Anisole was purified by vacuum distillation. Boiling point, 65°C. at 20 mm. $n_D^{21.8}$ 1.5153; given in the literature, 1.51503.

p-Xylene. Kahlbaum's product was used without purification. Melting point, 12–14°C.; given in the literature, 16°C.

Mesitylene. Eastman's product was used without purification. $n_D^{14.6}$ 1.5000; given in the literature, 1.4966.

Dibenzyl. This was made according to the directions of Cannizzaro and Rossi (4). The crude product was recrystallized three times from alcohol using charcoal. It was then recrystallized twice from purified ether. Melting point, 51.5–52.5°C.; given in the literature, 52.5°C.

Tolane. Stilbene dibromide was treated under a reflux condenser for eight hours with a slight excess of saturated alcoholic potassium hydroxide. The potassium bromide was filtered off and the liquid returned to the flask with addition of a small amount of solid potassium hydroxide for another eight hours. The product was poured into ice water; the oily layer was separated, dried, and distilled *in vacuo.* The tolane fraction was recrystallized from alcohol four times, twice vacuum distilled, and again crystallized from absolute alcohol. Melting point, 60°C.; given in the literature, 60°C.

Chloroquinone. A mixture of 30 g. of chlorohydroquinone, 300 cc. of purified ether, and 200 g. of finely divided lead dioxide was stirred for 10 minutes, after which the lead dioxide was filtered off and washed well with ether. The combined ethereal solutions were evaporated to a volume of

200 cc. and crude chloroquinone crystallized out by freezing in a carbon dioxide–ether bath. Repeated recrystallizations from absolute ether gave a product melting at 57°C. (literature, 57°C.).

Quinone. Crude quinone was purified by several sublimations. Melting point, 113.5–114.5°C.; given in the literature, 115.7°C.

Toluquinone. This was prepared from *o*-toluidine by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point, 67–67.5°C.; given in the literature, 69°C.

p-Xyloquinone. *p*-Xylidine was oxidized by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point, 123–124°C.; given in the literature, 125°C.

Durene and duroquinone. These substances were obtained in a pure state from Professor L. I. Smith, to whom we are very deeply grateful. The melting points and boiling points given are uncorrected. Refractive indexes were determined with an Abbé refractometer. All quinones were repurified just preceding use.

SUMMARY

1. The absorption spectra of chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone were measured quantitatively in the absence of solvent.

2. A technique is described for obtaining quantitative light absorption measurements on thin layers of liquids or melted solids.

3. The absorptions of equimolecular mixtures of the above quinones with aromatic hydrocarbons, ethers, and amines were measured. A variation in the effect of these "solvents" on the spectra of the quinones was observed, ranging from very pronounced color changes attributed to molecular compound formation to slight changes of the order of "solvent effects."

4. The changes from the absorption spectra of quinones in a pure state to the spectra in molecular compound forming "solvents" have been correlated with the known oxidation-reduction potentials of the quinones.

5. Two generalizations have been found:

I. In a series of quinones the change in the absorption spectrum brought about by a "solvent" capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.

II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

We wish to express our thanks to both the Physics Department and the Biophysics Department of the University of Minnesota for their valuable aid in supplying equipment and suggestions as to its use.

REFERENCES

(1) PFEIFFER, P.: Organische Molekulverbindungen Enke, Stuttgart (1927).

(2) CONANT AND FIESER: J Am. Chem. Soc **45**, 2208 (1923).

(3) Bur. Standards Scientific Paper No 440, p 129

(4) CANNIZZARO AND ROSSI Ann **121**, 250 (1862)

(5) NIETZKI: Ann. **215**, 159 (1882).

CHEMICAL ACTION IN THE GLOW DISCHARGE. XI

The Decomposition of Nitrogen Dioxide and the Nitrogen Dioxide Equilibrium

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Received May 9, 1933

INTRODUCTION

The present study of the decomposition of nitrogen dioxide in the glow discharge was undertaken for the purpose of determining the limiting yields as well as the principles underlying the fixation of nitrogen in the electric arc. Attention was also given to the mechanism of reaction involved.

APPARATUS AND METHOD

The apparatus and method of procedure were essentially the same as those used for the decomposition of nitrous oxide (1). A discharge tube of the type illustrated in figure 4 was enclosed in an electric furnace and the temperature maintained constant at 170°C., except in the experiment on the temperature coefficient. This temperature was chosen so that the gas would be entirely in the form of NO_2. Pressure changes were read with a Nujol oil manometer; the system was kept free of mercury vapor. The nitrogen dioxide was obtained from a reservoir of liquid nitrogen dioxide made by the arc process.

RESULTS

The discharge current

The relative rates of decomposition of nitrogen dioxide in the negative glow and positive column, as determined by the discharge current, are shown in figure 1. Line 1 is for the negative glow and line 2 for the negative glow and positive column combined. The difference between lines 1 and 2 gives the relative rate for the positive column alone, while the difference between lines 1V and 2V gives the potential drop in this region.

It will be observed that the rates are proportional to the current in both the negative glow and positive column. The yield measured from the slopes of the lines is 21 molecules decomposed per electron of current in the negative glow, 80 molecules per electron in the positive column and negative glow combined, and 59 in the positive column alone. The proportionality between current and rate shows this reaction to behave similarly to the other reactions described in this series.

The voltage curves 1V and 2V give an indication of the power consumed per molecule for various discharge currents. The conspicuous difference in the two regions of the discharge is that the rate is proportional to the power input in the negative glow, while in the positive column the voltage, and hence the power consumed, drops naturally as the current increases.

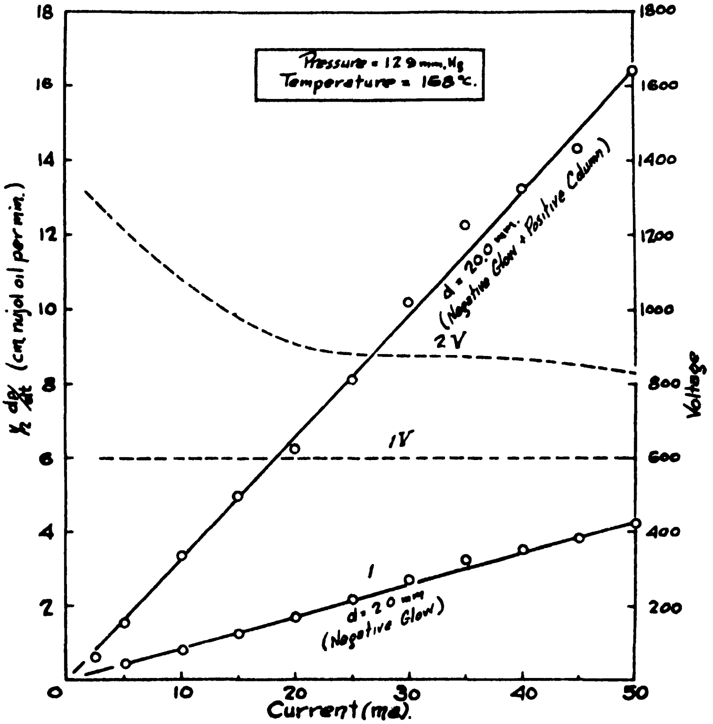

FIG. 1. RELATIVE RATES OF DECOMPOSITION OF NITROGEN DIOXIDE IN THE NEGATIVE GLOW AND POSITIVE COLUMN

The pressure

This reaction is again similar to the others studied in this series in that the rate of reaction in the negative glow is independent of the initial pressure of nitrogen dioxide between wide limits. The electrochemical equivalence law,

$$\frac{dP}{dt} = \alpha I$$

enunciated for the discharge is still applicable.

The effect of pressure in the positive column is difficult to determine since the power input and effective length of the column both vary with the pressure

The power efficiency

The power consumed per molecule decomposed in the various regions of the discharge is illustrated in figure 2

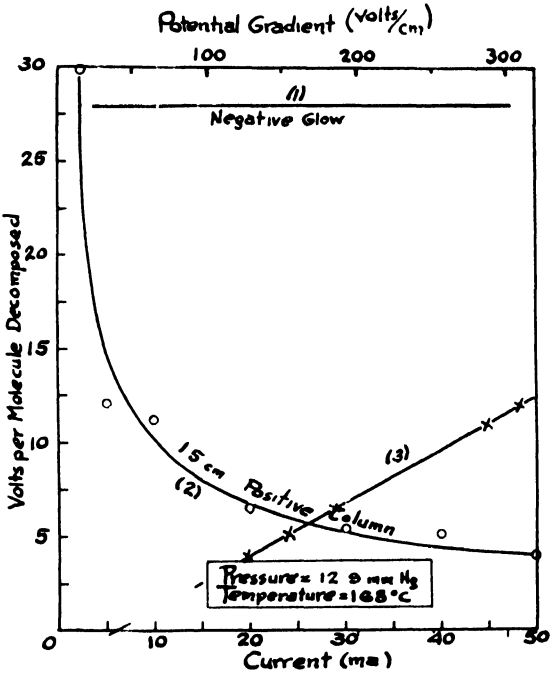

FIG 2 POWER CONSUMED PER MOLECULE DECOMPOSED IN THE VARIOUS REGIONS OF THE DISCHARGE

Line 1 shows the power consumption to be constant in the negative glow from 2 5 to 50 ma , and is equivalent to approximately 28 electron volts per molecule (V_e/M) decomposed

The results obtained in the positive column are shown by line 2 It will be noted that the efficiency changes from $V_e/M = 30$ at 2 5 ma current to $V_e/M = 4$ at 50 ma This increase in efficiency is due entirely to a decrease in potential gradient, since line 2 of figure 1 shows the rate to be proportional to the current

The change in efficiency with respect to potential gradient is shown by line 3, in which it will be seen that V_e/M decreases linearly with the potential gradient throughout the column; the gradients given are those obtained with the various discharge currents.

Foreign gases

The effect of foreign gases on the rate of decomposition is illustrated in figure 3.

Especial attention is called to the fact that nitrogen and oxygen are very similar in their effects on the rate of decomposition, oxygen if anything being slightly more efficient. The rate of decomposition is slowed down even less by helium than by oxygen.

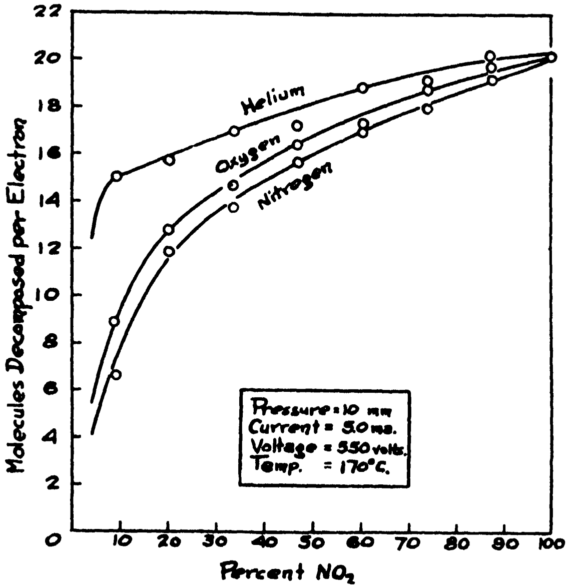

FIG 3. THE EFFECT OF FOREIGN GASES ON THE RATE OF DECOMPOSITION OF NITROGEN DIOXIDE

The above results are in distinct contrast to those obtained with nitrous oxide wherein the retardations in rate of dissociation in the presence of nitrogen, oxygen, and helium were proportional to the partial pressure of nitrous oxide times the relative probabilities of ionization (Θ) of their gases. In the case of nitrous oxide, therefore, these foreign gases contributed nothing to the rate of decomposition. To say in the present case that activated nitrogen, for instance, did not decompose nitrogen dioxide it would be necessary to assign values of $\Theta = 1$ to helium, $\Theta = 3$ to nitrogen, and $\Theta = 31$ to nitrogen dioxide, i.e., the probability for ionization in nitrogen dioxide must be over ten times that in nitrogen. Lind (2) assigns values to the stopping powers of these gases for α rays of 111 for nitrogen dioxide and 99 for nitrogen; thus the ionization efficiency in the two gases is nearly the same. It must be concluded, therefore, that an activated helium, oxygen, or nitrogen molecule is almost as effective in inducing decomposition as is an activated nitrogen dioxide molecule itself.

Temperature

The effect of temperature on the rate of dissociation is shown in figure 4. The runs were carried out at constant gas density from room temperature to 225°C. The voltage remained fairly constant over the entire temperature range.

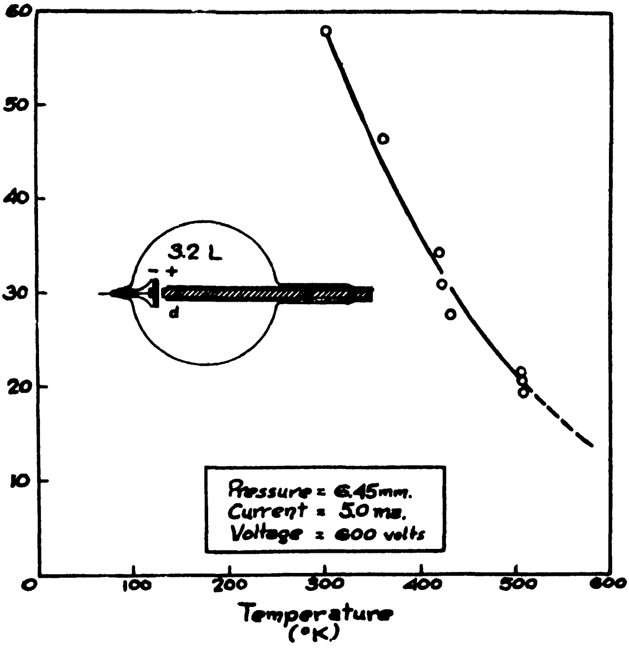

FIG. 4. THE EFFECT OF TEMPERATURE ON THE RATE OF DECOMPOSITION OF NITROGEN DIOXIDE

The conspicuous and surprising thing to note in these experiments is that the number of molecules decomposed per electron decreased almost linearly with temperature over the range investigated. At 225°C. about 30 electron volts are required to decompose one molecule, while at room temperature this value drops to 10 electron volts.

Equilibrium

The $2NO_2 \rightleftharpoons N_2 + 2O_2$ equilibrium was measured by running the discharge in a $N_2/2O_2$ mixture for about an hour at room temperature until equilibrium was established. The pressures ranged from 5 to 10 mm. of mercury. Liquid air was then applied to the discharge tube and the nitrogen dioxide frozen out. The nitrogen and oxygen were next pumped off, the nitrogen dioxide was allowed to evaporate, and the pressure measured with an oil manometer. The results showed the nitrogen dioxide pressure to be 1.6 per cent of the initial pressure.

The rate of synthesis of nitrogen dioxide in a liquid air-cooled tube of the type used in the decomposition experiments yielded 1.58 molecules of nitrogen dioxide per electron of current. Referring to figure 3 it will be seen that the rate of decomposition of nitrogen dioxide in a mixture containing approximately 1.5 per cent nitrogen dioxide and 98.5 per cent nitrogen or oxygen is equal to the observed rate of synthesis in a $N_2/2O_2$ mixture. The equilibrium value of 1.6 per cent nitrogen dioxide is, therefore, substantially correct.

DISCUSSION OF RESULTS

The general interpretation to be given to these results is necessarily the same as that applied to the other reactions studied in this series, namely, that the reaction is brought about by positive ions formed in the discharge. The first step in the decomposition process is the formation of an NO_2^+, and N_2^+ or an O_2^+ ion. The second step consists of the dissociation of nitrogen dioxide by the ion so formed.

A calculation of the number of molecules decomposed per ion in the negative glow can be made from an evaluation of the number of ions formed for each electron leaving the cathode. Since the positive ion current to the cathode is negligible (3), and since the electrons leaving the cathode receive an energy corresponding to the cathode potential drop, the number of positive ions formed per electron of current may be estimated directly from the results of Lehman (4) and of Anslow (5). Lehman obtained 13 ions per 600 volt electron, i.e., an expenditure of 45 volts per ion in nitrogen. Anslow, using a similar method, obtained a somewhat lower value of 5.9 ions for a 600 volt electron. Langmuir and Jones (6) obtained a value of about 85 volts per ion, which is equivalent to 7 ions per 600 volt electron.

Figure 3 shows 20 molecules of nitrogen dioxide to be decomposed per electron. According to Lehman's value, therefore, the number of molecules decomposed per NO_2^+ ion is $M/N = 20/13 = 1.55$. Anslow's value gives $M/N = 20/5.9 = 3.4$, while from Langmuir and Jones the ratio $M/N = 20/7 = 2.8$ is obtained. It will be seen from this that an estimation of the M/N ratio necessarily involves an uncertainty factor of 2. Since the results of Lehman appear the most consistent, it is probable that the correct value at 170°C. is $M/N = 1.55$ or possibly 2. At room temperature, however, the M/N ratio is approximately three times that for 170°C.

An estimation of the M/N ratio in the positive column is speculative, since there exists no reliable method for computing the number of ions formed per electron of current. Assuming the same voltage efficiency in the positive column as in the negative glow a ratio of $M/N = 10$ is obtained at 50 ma. current. This value is necessarily high but serves as an upper limit. At 2.5 ma. the ratio falls to $M/N = 1.5$. It is reasonable to assume, therefore, that the true M/N ratio is essentially the same in the two regions of the discharge.

The results presented in the series of studies on the synthesis and decomposition of nitrogen dioxide in the discharge show directly the limits that may be obtained in the arc process for the fixation of nitrogen. In the synthesis (7) it has been shown that it is possible to remove the nitrogen dioxide from the arc as fast as formed by cooling the discharge tube with liquid air. In this case the reaction $N_2 + 2O_2 = 2NO_2$ goes to completion. The great source of energy loss results from the fact that only N_2^+ ions contribute to the formation. On the other hand it is to be seen from the present paper that N_2^+, O_2^+, and NO_2^+ ions all contribute to dissociation, hence the rate of dissociation is rapid compared to synthesis. For this reason the equilibrium value is low, being of the order of 1.6 per cent nitrogen dioxide. Thus the lower limit for the above equation is 1.6 per cent on the side of nitrogen dioxide where the rates of synthesis and decomposition are equal, and 100 per cent when decomposition is eliminated. In practice, therefore, the yield must depend on the rapidity with which nitrogen dioxide is removed from the discharge. It is interesting to note that the equilibrium will be practically the same in air as in an $N_2/2O_2$ mixture, since both the rates of synthesis and decomposition are the same under these conditions.

MECHANISM OF REACTION

There are two probable mechanisms for the reaction about the ion when once formed. One is the step or quasi molecule mechanism, generally considered in photochemical reactions. It involves dissociation according to the equation:

$$NO_2 \rightarrow NO + O$$

This step is impossible in the present case since it would necessitate a retardation in rate by oxygen; the possibility of nitric oxide being decomposed before being carried out of the discharge by convection is small. Figure 3 shows the dissociation in oxygen to be slightly greater than in nitrogen. Again such a mechanism would demand a positive and not a negative temperature coefficient since the rate of oxidation of nitric oxide increases with decreasing temperature. It must be concluded, therefore, that the production of nitric oxide is not a step in the reaction mechanism.

The second possible mechanism for decomposition is one involving ion clusters. An ion cluster of the form ($NO_2^+ NO_2$) or ($N_2^+ \cdot 2NO_2$) is considered as decomposing directly into $N_2 + 2O_2$. This mechanism is in accord with the observed negative temperature coefficient since the dielectric constant, and hence the clustering ability of nitrogen dioxide, increases with decreasing temperature. It is interesting to note that the presence of such clusters has been shown to exist in mixtures of nitrogen and oxygen by mass spectrograph measurements by Luhr (8). The cluster mechanism will be discussed in more detail in a later communication.

SUMMARY

The decomposition of nitrogen dioxide in the glow discharge is shown to obey the same electrochemical equivalence law given for the other reactions studied in this series.

The decomposition is shown to be brought about with almost equal ease by NO_2^+, N_2^+, O_2^+, and He^+ ions.

The M/N ratio at 170°C. is calculated for the negative glow and positive column. The ratio lies between $M/N = 1.55$ and $M/N = 3$. The lower value is the more probable.

The decomposition has a strong negative temperature coefficient, the M/N ratio being three times as large at room temperature as at 225°C.

A value of 1.6 per cent is obtained for the amount of nitrogen dioxide in the arc at room temperature under equilibrium conditions. This is discussed in connection with the possible yields that can be obtained in the arc process for nitrogen fixation.

The results are interpreted as indicating that the decomposition cannot be by step mechanism involving the formation of nitric oxide. It is suggested that the cluster type mechanism will best account for both the rate decomposition and the negative temperature coefficient.

REFERENCES

(1) Kueck, P. D., and Brewer, A. K.: J. Phys. Chem. **34**, 2395 (1932).
(2) Lind, S. C.: Chemical Effects of Alpha Particles and Electrons. The Chemical Catalog Co., New York (1921).
(3) Brewer, A. K., and Miller, R. R.: Phys. Rev. **42**, 786 (1932).
(4) Lehman, J. F.: Proc. Roy. Soc. London **115**, 624 (1927).
(5) Anslow, G. A : Phys. Rev. **25**, 484 (1925).
(6) Langmuir, I., and Jones, H. A.: Phys. Rev. **31**, 357 (1928).
(7) Westhaver, J. W., and Brewer, A. K.: J. Phys. Chem. **34**, 554 (1930).
(8) Luhr, O.: Phys. Rev. **38**, 1937 (1931).

CHEMICAL ACTION IN THE GLOW DISCHARGE. XII

The Dissociation of Ammonia[1]

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The catalytic, alpha ray, and photochemical decomposition of ammonia have been so extensively discussed in the recent literature that it has seemed advisable to contrast these results with those obtained in the glow discharge.

APPARATUS AND METHOD

In general the method of procedure in this work is similar to that used for the decomposition of nitrous oxide (1). The types of discharge tubes used are illustrated in the inset to figure 1 of this paper and figure 1A of the nitrous oxide paper. The temperature coefficient was obtained by enclosing the entire tube (figure 1A) in an electric oven. The pressure changes were read with a McLeod gauge, or with a Nujol oil differential manometer. The gases used were purified and stored as described in previous articles of this series.

The rate of reaction was determined from the initial slope of the line in time vs. pressure curves. Since the curves were usually straight lines over the first half of the pressure rise little difficulty was experienced in obtaining accurate initial rates.

RESULTS

The effect of ammonia pressure

The rate of decomposition at various initial pressures of ammonia is given in table 1.

It will be noted that the rate of reaction, R, as well as the efficiency, M/V, remain constant from below 4 mm. to about 16 mm. The efficiency varies little at lower pressures, although the rate and voltage both increase. At pressures above 16 mm. the appearance of the discharge changes entirely. The general glow disappears and thread-like arcs appear between the electrode; under these conditions the efficiency at least doubles.

The independency of the rate on the ammonia pressure between wide limits shows this reaction to be similar to others studied in this series. The enhancement of the rate accompanying the change in appearance of the discharge and drop in the cathode potential above 16 mm. is unique to ammonia decomposition. This peculiar behavior in ammonia is doubtless occasioned by its remarkable ability to lower the cathode potential drop by changing the "work function" of the surface.

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[1] This work was carried out under the direction of Dr. A. Keith Brewer.

The fact that the rate is independent of the pressure has an analogue in the photochemical decomposition, where Wiig and Kistiakowsky (2) have shown the quantum yield to be independent of the pressure from 800 to 1 mm.

TABLE 1

Rate of decomposition at various initial pressures of ammonia

PRESSURE OF AMMONIA	RATE	V (cathode fall)	M/e (molecules per electron)	V/M (electron volts per molecule)
mm Hg	*mm per minute*			
0 5	0 284	718	4 72	152
4 0	0 138	331	2 34	141
16 0	0 138	339	2 34	145
32 0	0 220	253	3 74	67 6

The discharge current

The effect of current on the rate of decomposition in the negative glow and in the negative glow and positive column combined is shown in figure 1. It will be noted that the rate is proportional to the current in both regions of the discharge. This, combined with the independence of rate on pressure, enables the decomposition to be expressed by the simple equation $dP/dt = \alpha I$, as in the case of all other reactions studied in the glow discharge. A linear current relationship was also obtained by Davies (3), using Siemens' type of discharge.

The significant point to note in these results is that the proportionality between current and rate is a direct indication that the decomposition is a primary process; the initiation of the reaction, therefore, results from a direct collision between an electron and an ammonia molecule, or some other molecule capable of inducing decomposition. The initial and rate-determining steps cannot, therefore, involve any interaction between activated states.

Added gases

The rates of dissociation of ammonia in the negative glow in the presence of various gases are given in table 2.

The values for the electron volts required to dissociate one molecule (V/M) show only a small gradual increase up to 80 per cent added gas in

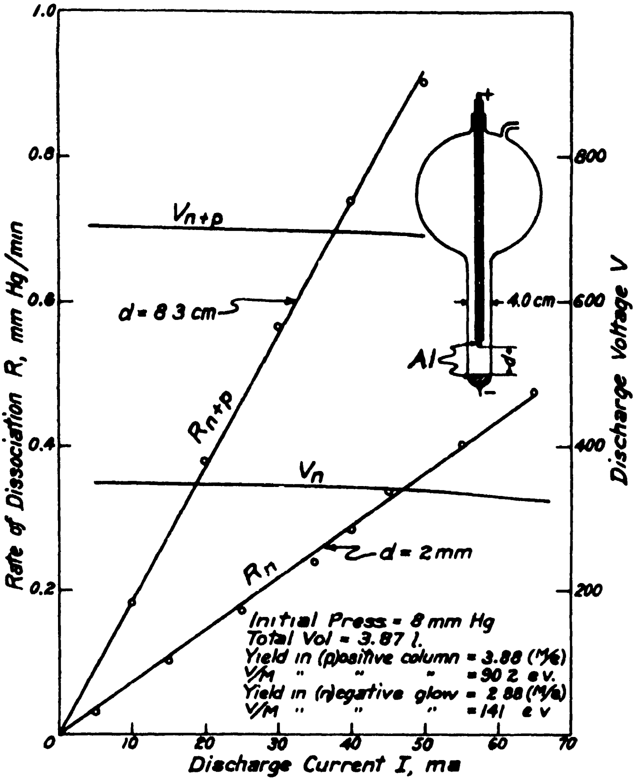


FIG. 1. EFFECT OF CURRENT ON THE RATE OF DECOMPOSITION

R_n and V_n give rate and voltage in negative glow; electrode separation 2 mm. R_{n+p} and V_{n+p} give rate and voltage in combined negative glow and positive column; electrode separation 8.2 cm.

TABLE 2

Rates of dissociation of ammonia in the negative glow in the presence of various gases

ADDED GAS	RATE	V (cathode fall)	M/V	V/M (electron volts per molecule)
	mm per minute			
None	0.214	390	3.42	114
80 per cent nitrogen	0.174	400	2.78	144
80 per cent hydrogen	0.086	430	1.38	312
80 per cent ($N_2 + 3H_2$)	0.162	385	2.59	155
80 per cent helium	0.174	420	2.78	151
80 per cent argon	0.176	315	2.82	112
50 per cent oxygen	0.221	415	3.32	125

every case except for hydrogen. Above 80 per cent the rate in all cases drops rapidly to zero at 100 per cent added gas. It follows, therefore, that ions of these various gases are about as efficient catalysts for the decomposition of ammonia as are NH_3^+ ions themselves. In the case of hydrogen, however, the rate decreases for various partial pressures of added hydrogen in proportion to the number of H_2^+ ions present. Indeed, the computed curve for the number of NH_3^+ ions formed as given by the relative ionizing efficiency of an electron in ammonia and hydrogen mixtures follows the rate curve almost exactly in a manner analogous to that shown in figure 7 of paper XI of this series (4). It must be concluded, therefore, that H_2^+ ions do not catalyze the decomposition. The retarding effect of hydrogen cannot be due to the interaction of hydrogen atoms, and NH or NH_2 as is postulated in the photochemical decomposition by Melville (5) since the absence of N_2H_4 in the negative glow, as later described, suggests the absence of NH and NH_2. Again this mechanism demands that $H + NH_2 \rightarrow NH_3$ increase with the square of the current if the production of H and NH_2 are each proportional to the current; the observed dissociation, however, is proportional to the current. It should be added that convection was sufficiently rapid so that the chance of a quasi molecule such as NH_2 being struck by an electron before being carried out of the path of the discharge was negligible.

TABLE 3

The effect of Hg^+ *ions on the decomposition of ammonia*

TEMPERATURE	PRESSURE	PER CENT Hg	RATE	M/e (molecules per electron)	V/M (electron volts per molecule)
degrees C	*mm*		*mm per minute*		
25	5.95	0	0.236	3.54	110
163	9.55	19	0.211	2.45	153
191	12.9	37	0.276	3.05	130

Oxygen up to a partial pressure of 75 per cent behaves in a manner identical to that of nitrogen or argon. Above this pressure the rate falls rapidly to zero. Since the oxidation of ammonia to nitrogen dioxide and water would show a decrease in pressure, and since the oxidation of the hydrogen alone would show only a slight increase, it seems likely, in view of the large pressure increase observed, that O_2^+ ions dissociate ammonia in a manner similar to N_2^+ and A^+ ions, and that no appreciable oxidation of the ammonia occurs under 75 per cent oxygen. In this respect oxygen in the negative glow behaves less effectively than in the photochemical decomposition described by Taylor and Salley (6) in which they found the rate to be increased some fourfold by oxygen. The fact that O_2^+ ions do not react with the hydrogen to form water is not surprising, as it has been shown that this reaction is initiated entirely by H_2^+ ions, the O_2^+ ions being inert (7). Since only initial rates were used, the production of H_2^+ ions was negligible.

In determining the effect of Hg^+ ions it was necessary to vary the temperature to give different mercury pressures. The results obtained are given in table 3.

Since these data could not be obtained under constant conditions, some scattering in the value of V/M is to be expected. The results indicate, however, that Hg^+ ions behave similarly to N_2^+ ions in catalyzing decomposition. The ionization potential of mercury being considerably lower than that of ammonia suggests that it is not necessary for the charge to be transferred to the ammonia molecule for decomposition to occur about the ion.

Equilibrium

The ammonia synthesized at room temperature in a discharge, run in an N_2 $3H_2$ mixture until equilibrium was established, was frozen out with liquid air, and the nitrogen and hydrogen were pumped off. The ammonia was then allowed to evaporate and the pressure was read. The ammonia so formed represented an average of 5.55 per cent of the initial amount by volume. The amount of ammonia remaining from a similar test, starting with pure ammonia, was 6.56 per cent. Thus the most probable value for the equilibrium at room temperature in the negative glow is about 6 per cent.

This equilibrium value is in agreement with 6 per cent reported by Davies (3) for the Siemens' tube, but is somewhat higher than the alpha ray value, 4.7 per cent, obtained by d' Olieslager and Jungers (8).

Reaction products

The total pressure increase invariably showed the final decomposition to go almost completely to nitrogen and hydrogen. Attempts were made to detect hydrazine by immersing the discharge in dry ice and alcohol. No hydrazine was frozen out in the negative glow; in the positive column, however, at 1 mm. pressure and 20 ma. current, a condensible product was obtained equivalent to one molecule for every ten ammonia molecules decomposed. At 8 mm. pressure no condensible product could be detected, nor could any be detected at any pressure when dry ice was applied to the discharge tube after the ammonia had been 50 per cent or more decomposed.

These results indicate that the decomposition ordinarily goes to instantaneous completion in the discharge. In this respect they differ from the findings of Bredig, Koenig, and Wagner (9), who obtained as high as 80 per cent conversion to hydrazine at low pressures and high current densities when ammonia was drawn through the discharge. Gedye and Allibone (10) obtained appreciable quantities of hydrazine with cathode rays at low pressures. The results are in agreement in that in all cases low pressures favored the production of hydrazine.

The temperature coefficient

The influence of temperature on the number of molecules dissociated per electron (M/e) is shown by curves 1, 2, and 3 of figure 2. Each curve was taken at constant gas density; the voltage did not change with temperature.

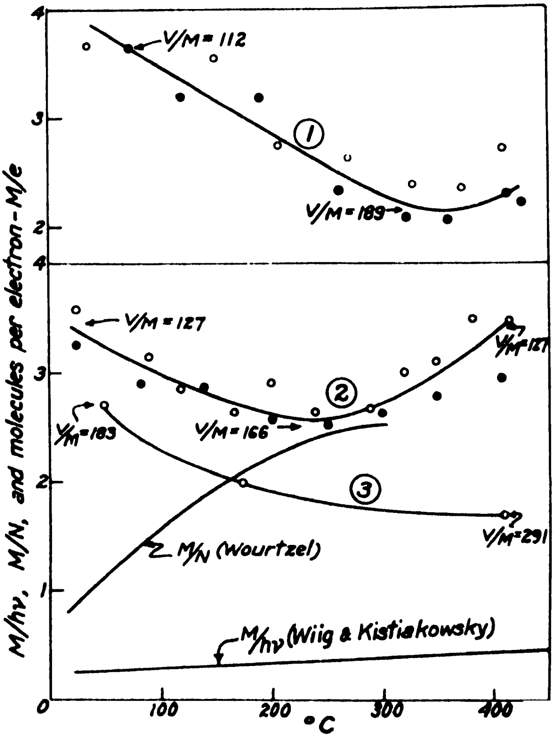


FIG. 2. EFFECT OF TEMPERATURE ON THE RATE OF DISSOCIATION

Curve 1: $P = 1.3$ mm. at 25°C., $I = 5$ ma, $V = 415$ volts.

Curve 2: $P = 5.5$ mm. at 25°C., $I = 20$ ma., $V = 431$ volts.

Curve 3: $P = 5.5$ mm. $NH_3 - H_2$ mixture at 25°C., $I = 20$ ma, $V = 495$ volts.

The curves show a temperature coefficient of less than unity, i.e., about 0.983 per 10°C. The coefficient becomes unity for curves 1 and 2 at 350°C. and 250°C., respectively, and shows a positive value at still higher temperatures; curve 3, with 50 per cent hydrogen, is less than unity throughout the entire temperature range.

The results of Wourtzel (11) for alpha rays and those of Wiig and Kistiakowsky (2) for photochemical dissociation are also shown for comparison.

Kuhn (12) obtained a temperature coefficient for photochemical decomposition comparable to that given by Wourtzel, but observed a retarding effect in hydrogen similar to curve 3.

The fact that curve 1 shows a more pronounced decrease in rate than does curve 2, indicates that the decrease in rate with temperature is encouraged by low pressures. Probably it is for this reason that the present results differ from those of Wourtzel.

The cathode surface

The results which have been discussed so far have been for a "worked in" cathode. This particular reaction shows a far greater cathode aging effect than that usually encountered in the discharge (13). For instance, a freshly machined aluminum cathode gave a rate of 0.203 mm. per minute with a potential drop between the electrodes of 292 volts. This is equivalent to 84 electron volts per molecule dissociated. As the cathode aged the voltage increased while the rate decreased for a period of about three hours, after which the conditions remained fairly constant. The values for a worked-in cathode are given in figure 2; it will be noted that at room temperature from 112 to 127 electron volts are required per molecule.

An interesting side light to the above aging effect is that running the discharge in pure oxygen or hydrogen has no effect on the worked-in conditions, although a discharge in water vapor readily restores the original freshly machined characteristics. This is doubtless due to the reduction of a nitride film on the cathode, the formation of which is responsible for the aging effect.

The high rate of dissociation observed with freshly machined cathodes is intimately connected with the adsorption of ammonia on the surface, since under the conditions for high rate an abnormally low cathode potential drop was observed. The cathode potential drop is determined directly by the "work function" of the surface, being in general about one hundred times the work function. Brewer (14) has shown that the work function of a surface may be lowered from a third to a half by the adsorption of ammonia; this has been accounted for by the dissociation of the ammonia into ions by the surface forces. Since the lowering of the work function increases the ease with which electrons are emitted from the cathode, it should enhance the efficiency of the discharge.

A further possibility of accounting for the abnormally high rates on fresh surfaces may be had in the observation of Brewer that the ammonia adsorbed on metallic surfaces can undergo decomposition at a temperature as low as 250°C. While the surface was cold in the present case, it is probable that the bombardment by positive ions, atoms, and metastable molecules received by the cathode during the discharge would be as efficient as a hot surface in dissociating the adsorbed ammonia.

DISCUSSION OF RESULTS

The results just presented are similar to those previously obtained in the discharge, in that the rate is proportional to the current and independent of the pressure between wide limits. They possess two distinct differences, however, from those observed in the decomposition of nitrous oxide. The first is the pronounced cathode "working-in" effect already discussed. The second is in the effect of foreign gas ions. In the case of nitrous oxide the rate was determined solely by the rate of production of N_2O^+ ions; all other ions were without effect. In the present case, however, decomposition occurs almost as readily around N_2^+, O_2^+, He^+, A^+, and Hg^+ ions as about NH_3^+ ions; only H_2^+ ions are inert.

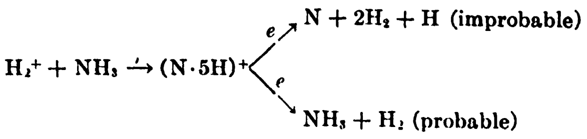
It is interesting to note that decomposition occurs about Hg^+ ions although the ionization potential of mercury is some 3 volts below that of ammonia. Thus it follows that a transfer of charge from the foreign ion to ammonia is unnecessary.

A determination of the number of molecules decomposed per ion (M/N) involves an uncertainty factor of 2, since various observers are in disagreement to this amount regarding the number of ions formed by an electron having an energy equal to the cathode fall of potential. Lehmann (15) gives 8 as the number of positive ions formed by a 350 volt electron. Anslow (16) obtained but 3.5 ions per 350 volt electron. The number of molecules decomposed per electron at 1.3 mm. is 3.7; the ratio, therefore, is $M/N = 3.7/8 = 0.46$, using the value of Lehmann, and $M/N = 3.7/3.5 = 1.1$ from Anslow's value. At somewhat higher pressures and especially at higher temperature the M/N ratio decreases from the values just given. Lind (17) gives $M/N = 0.8$ at room temperature. The best that can be said, therefore, is that the ratio is low, lying between 0.5 and 1.0.

MECHANISM OF DECOMPOSITION

The fact that the M/N ratio is less than 1.0 indicates either that all of the NH_3^+ ions do not undergo decomposition, or that there is an appreciable synthesis. The latter possibility is obviously impossible for initial rates and is not appreciable most of the time of a run, as can be seen from the equilibrium results. On the other hand, the inability of ions to cause dissociation can be accounted for on the basis of a cluster type of reaction mechanism.

An ion cluster upon disintegration may dissociate according to probability into its original constituents or into some new form. The data show that ammonia is not appreciably decomposed by H_2^+ ions; the formation and dissociation of the cluster, therefore, can be expressed by the process:



$$H_2^+ + NH_3 \rightarrow (N\cdot 5H)^+ \begin{cases} \xrightarrow{e} N + 2H_2 + H \text{ (improbable)} \\ \xrightarrow{e} NH_3 + H_2 \text{ (probable)} \end{cases}$$

In the cluster N is surrounded by 5 H; hence the chance for return to ammonia is high.

The conditions about N_2^+, He^+, A^+, O_2^+, and NH_3^+ ions are materially different. Thus

$$N_2^+ + NH_3 \rightarrow (3N\cdot 3H)^+ \begin{array}{l} \xrightarrow{c} N_2 + N + H_2 + H \text{ (probable)} \\ \xrightarrow{c} NH_3 + N_2 \text{ (small probability)} \end{array}$$

and

$$NH_3^+ + NH_3 \rightarrow (2N\cdot 6H)^+ \begin{array}{l} \xrightarrow{c} N_2 + 3H_2 \text{ (probable)} \\ \xrightarrow{c} 2NH_3 \text{ (probable)} \end{array}$$

In these two cases the N is not completely surrounded by H; the possibility of ammonia splitting out of the cluster, therefore, is much smaller than for the H_2^+ ion clusters.

SUMMARY

1. Ammonia is shown to decompose into the elements in the glow discharge. Some hydrazine is formed in the positive column but none in the negative glow.

2. The rate of decomposition is proportional to the current and independent of the pressure.

3. The ability of ammonia to dissociate into ions on the cathode surface results in abnormal reaction rates at higher pressures and for freshly machined surfaces.

4. The equilibrium between NH_3 and $N_2/3H_2$ is approximately 6 per cent NH_3.

5. Decomposition is not appreciably retarded by N_2, A, He, O_2 and Hg up to 80 per cent added gas. H_2 retards the rate in proportion to the number of H_2^+ ions present.

6. The decomposition exhibits a less-than-unity temperature coefficient below 250°C. Above this temperature a small increase in rate exists at the higher pressures.

7. The M/N ratio lies between 0.5 and 1.0.

8. The mechanism of decomposition about the ions is discussed.

REFERENCES

(1) Kueck, P. D., and Brewer, A. K.: J. Phys. Chem. **36**, 2395 (1932).
(2) Wiig, E. O., and Kistiakowsky, G. B.: J. Am. Chem. Soc. **54**, 1806 (1932).
(3) Davies, J. H.: Z. physik. Chem. **64**, 657 (1908).

(4) Brewer, A. K., and Kueck, P. D.: J. Phys. Chem. **37,** 889 (1933).
(5) Melville, H. W.: Trans. Faraday Soc. **28,** 885 (1932).
(6) Taylor, H. S., and Salley, D. J.: J. Am. Chem. Soc. **55,** 96 (1933).
(7) Brewer, A. K., and Westhaver, J. W.: J. Phys. Chem. **34,** 2343 (1930).
(8) d'Olieslager, J. F., and Jungers, J. C.: Bull. soc. chim. Belg. **40,** 75 (1931).
(9) Bredig, G., Koenig, A., and Wagner, O. H.: Z. physik. Chem. **139,** 211 (1928).
Koenig, A., and Wagner, O. H.: Z. physik. Chem. **144,** 213 (1929).
(10) Gedye, G. R., and Allibone, T. E.: Proc. Roy. Soc. London **130,** 346 (1931).
(11) Wourtzel, E.: Le radium **11,** 332 (1919).
(12) Kuhn, W.: J. chim. phys. **23,** 521 (1926); Compt. rend. **177,** 956 (1923).
(13) Kueck, P. D., and Brewer, A. K.: J. Phys. Chem. **35,** 3207 (1931).
(14) Brewer, A. K.: J. Am. chem. Soc. **54,** 1888 (1932); **54,** 4588 (1932).
(15) Lehmann, J. F.: Proc. Roy. Soc. London **115,** 624 (1927).
(16) Anslow, G. A.: Phys. Rev. **25,** 484 (1925).
(17) Lind, S. C.: Chemical Effects of Alpha Particles and Electrons. The Chemical Catalog Co., New York (1921).

CONDUCTIVITY MEASUREMENTS OF THORIUM AND OTHER JELLY-FORMING SYSTEMS

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In an important communication by Laing and McBain (1), it has been shown that sol and gel of one and the same substance are identical in their electrical conductivity, lowering of vapor pressure, refractive index, and some other minor properties. However, in the case of curds they found a marked drop in conductivity and osmotic activity. In previous publications from this laboratory, an attempt has been made to investigate various properties of inorganic jellies, for example, the viscosity and hydrogen-ion concentrations during the course of jelly formation (2), the syneresis of various jellies (3), the thixotropy (4), the changes in extinction coefficients (5), and the influence of various factors on the formation of jellies (6). In this communication, some observations have been made regarding the conductivity of some typical jellies such as thorium arsenate, thorium phosphate, thorium molybdate, ferric arsenate, and aluminum hydroxide.

EXPERIMENTAL

The jellies of thorium arsenate, thorium phosphate, and thorium molybdate were prepared by the method described by Prakash and Dhar (7). To thorium nitrate solution containing 12.5 g. of the salt in 250 cc. (23.54 g. of ThO_2 per liter), suitable concentrations of potassium arsenate, phosphate, or molybdate were added, and the changes in the conductivities during the course of gelation of these systems were investigated from time to time by the Hartmann and Braun roller bridge arrangement. The temperature was kept constant at 35°C. The observations have been recorded in table 1.

The results recorded in this table show that in the case of thorium arsenate, the mixture of thorium nitrate and potassium arsenate attains an equilibrium within thirty minutes, and after that the conductivity remains fairly constant up to the point of setting. As the opalescence increases, there is a slight decrease in the conductivity, the maximum decrease being obtained in the course of twenty-four hours when the jelly becomes almost opaque. The jelly on further aging, however, shows again an increase in the conductivity.

In the case of transparent jellies like thorium phosphate and thorium molybdate, when the mixture has once attained the equilibrium, the conductivity becomes constant. Even after the setting of the jellies, the conductivity does not change for a few hours. However, if the aging is allowed to continue, the conductivity also increases. The aging influence is less marked in the case of molybdate jelly.

TABLE 1

Conductivities of thorium jellies

Thorium nitrate solution = 10 cc

Total volume = 12 5 cc.

	THORIUM ARSENATE 1 cc of 18 per cent KH_2AsO_4	THORIUM PHOSPHATE 0 75 cc of 20 per cent KH_2PO_4	THORIUM MOLYBDATE 1 5 cc of 6 per cent K_2MoO_4
Time of setting	60 minutes	60 minutes	40 minutes
Nature of the jelly	Opalescent jelly is obtained from clear solution The opalescence increases continuously with time even after setting	Opalescent mixture giving clear solution and finally a transparent jelly	Opalescent mixture giving clear solution and finally a transparent jelly
Time	Conductivity of the jellies in mohs × 10^{-3}		
0	4 255	3 710	2 385
5 min	—	—	2 398
10 min.	—	3 635	—
15 min	4 264	—	2 395
20 min	—	3 616	—
25 min		—	2 390
30 min	4 297	—	—
40 min.		3 616	2 385
60 min	4 297	3 616	2 385
100 min.	4 297	3 615	—
120 min	4 285		—
180 min	—	—	2 385
200 min		3 654	—
260 min	—	3 698	—
24 hrs.	4 142	3 855	2 385
48 hrs	4 174	3 946	2 482
72 hrs	—	—	2 451
96 hrs	4 272	—	—

The influence of temperature on the conductivity of the above aged jellies has also been investigated. As the jellies were obtained by mixing the solutions of thorium nitrate with solutions of potassium arsenate, phosphate, or molybdate, the conductivities of these component solutions have also been measured at various temperatures. The concentrations of the solutions taken were the same as were necessary to give the above jellies. The results are given in table 2.

The results recorded in table 2 show that the temperature coefficients of the conductivities of thorium nitrate, potassium arsenate, potassium phosphate, and potassium molybdate are more regular, amounting to 2 per cent of the original conductivities at 35°C., as is usually found when Kohlrausch's expression is applied to electrolytes. The temperature coefficient of thorium arsenate jelly varies irregularly from 0.9 to 1.4 per cent of the original conductance; that of thorium phosphate is 1.54 per cent, and that of thorium molybdate 2 per cent of the original.

TABLE 2

Conductivities of component solutions

Thorium nitrate solution, 10 cc diluted to 12 5 cc ; potassium arsenate, 18 per cent solution, 1 cc in 12 5 cc of water; potassium phosphate, 0 75 cc. of 20 per cent solution in 12 5 cc water; potassium molybdate, 1 5 cc of 6 per cent solution in 12 5 cc. water

TEMPERATURE	CONDUCTIVITIES IN MHOS $\times 10^3$						
	Thorium nitrate	Potassium arsenate	Thorium arsenate jelly	Potassium phosphate	Thorium phosphate jelly	Potassium molybdate	Thorium molybdate jelly
degrees C							
35	2 433	0 8463	4 272	0 1471	3 946	0 8245	2 450
40	2 673	0 9263	4 522	0 1595	4 238	0 9095	2 713
45	2 913	1 011	4 739	0 1731	4 484	0 9766	2 925
50	3 132	1 074	4 932	0 1879	4 834	1 066	3 178
55	3 370	1 165	5 217	0 2032	5 168	1 137	3 418
60	3 616	1 254	5 508	0 2153	5 467	1 226	3 659
Temperature coefficient (approximate)	0 048	0 0163	0 049	0 0028	0 061	0 0166	0 048

TABLE 3

Changes in conductivity of ferric arsenate jelly on aging

TIME	CONDUCTIVITY
days	*mhos* $\times 10^3$
1	4 601
3	4 853
4	4 952
5	5 056

One thing which appears to be of interest is that the conductivities of the jellies of thorium arsenate and thorium phosphate are much greater than the total conductivities of the initial components. In the case of thorium molybdate, the conductivity of the jelly is slightly less than the additive conductivities of thorium nitrate and potassium molybdate. These results are discussed later on.

Ferric arsenate jelly

A positively charged sol of ferric arsenate, prepared by Holmes' method (8), containing 51.06 g. of ferric arsenate per liter and 0.028 *N* in chloride ions showed the following changes in conductivity on aging as it gained in the viscosity.

TABLE 4

Variation in conductivity with time

Conductivity of 10 cc of solution with 2 cc of water at 35°C = 4 031 × 10^{-3}

TIME	CONDUCTIVITY
	mhos × 10^{-3}
0	5 865
10 min.	5 865
30 min	5 865
2 hrs	5 865
1 day	6 163

TABLE 5

Influence of temperature on the conductivity of ferric arsenate sol and jelly

TEMPERATURE	CONDUCTIVITIES IN MHOS × 10^{-3}	
	Sol	Jelly
degrees C		
35	4 056	6 163
40	4 404	6 665
45	4 814	7 235
50	5 223	7 852
55	5 454	8 170
Temperature coefficient (approximate)	0 07 to 0 08	0 063 to 0 10

To 10 cc. of the sol of the first day were added 1 cc. of *N*/5 potassium chloride and 1 cc. of water. The jelly set in 30 minutes. The conductivity showed the variation with time given in table 4

Thus there is no variation in the conductance during and after gelation. However, the jelly undergoes marked aging and gains in conductivity on keeping for a longer time.

The influence of temperature on the conductivities of 2 days old sol (10 cc. of sol with 2 cc of water) and the above one day aged jelly is given in table 5.

On account of the presence of potassium chloride, the jelly is more conducting than the sol. The temperature coefficient of the sol is a little less than 2 per cent of the original conductance per degree, while in the case of the jelly, it is 1 to 1.4 per cent of the original.

Aluminum hydroxide jelly

An aluminum hydroxide sol was prepared by Crum's method. The sol dialyzed for seven days contained 10.48 g. of Al_2O_3 per liter. The jelly was obtained by adding 1 cc. of $N/10$ potassium chloride and 1 cc. of water to 10 cc. of the sol. From the clear sol, a transparent jelly accompanied with slight opalescence was obtained in the course of one hour. The changes with time during the gelation period and after are given in table 6. The conductivity of the sol previous to the addition of potassium chloride (10 cc. of sol + 2 cc. of water) was 1.120×10^{-4}. During the course of gela-

TABLE 6

Changes of conductivity with time during and after gelation period

Temperature = 35°C.

TIME	CONDUCTIVITY
	mhos × 10^{-3}
0	1.477
10 min.	1.456
20 min.	1.456
60 min	1.456
1 day	1.460
2 days	1.492
3 days	1.505

TABLE 7

Influence of temperature on the conductivity of aluminum hydroxide sol and jelly and of potassium chloride

TEMPERATURE	CONDUCTIVITIES IN MHOS × 10^{-3}		
	Sol	Potassium chloride	Jelly
degrees C			
35	0.1120	1.409	1.506
40	0.1247	1.539	1.655
45	0.1343	1.663	1.778
50	0.1455	1.794	1.914
55	0.1549	1.871	2.061
60	0.1675	—	2.213
Temperature coefficient (approximate)	0.00215	0.026	0.03

tion the conductivity remains fairly constant. However an increase is observed on aging.

The temperature influence on the conductivity of the following systems has also been investigated (see table 7):

1. 10 cc. of aluminum hydroxide sol mixed with 2 cc. of water.
2. 1 cc. of $N/10$ potassium chloride with 11 cc. of water.
3. 10 cc. of sol mixed with 1 cc. of $N/10$ potassium chloride and 1 cc. of water to give a jelly in 60 minutes. The jelly was allowed to age for three days before the temperature influence was studied.

Thus the conductivity of the jelly is almost additive of the conductivities of the sol and of the electrolyte. On the whole, the jelly is slightly less conducting than the components taken together. The temperature coefficient in all the three cases is per degree about 2 per cent of the original at 35°C.

DISCUSSION

The results recorded in the foregoing pages show the following facts:

The conductivity of thorium arsenate goes on decreasing with time as the opalescence increases up to a limit, when the jelly becomes completely opaque. Afterwards the jelly undergoes aging and the conductivity increases. The transparent jellies of thorium phosphate and thorium molybdate, once the equilibrium has been attained between the reactants, do not show any marked variation in the conductivities during the course of jelly formation. After a day or so, however, their conductivities begin to increase on aging. A similar behavior is observed with aluminum hydroxide and ferric arsenate jellies.

The conductivities of thorium arsenate and thorium phosphate jellies are greater than the conductivities of their initial components of the same concentrations, taken together. In the case of thorium molybdate, the conductance of the jelly is less than the additive conductances of thorium nitrate and potassium molybdate. The conductivity of aluminum hydroxide jelly is also slightly less than the additive values of aluminum hydroxide sol and the coagulant, potassium chloride.

The temperature coefficients per degree for the conductances of thorium nitrate, potassium arsenate, potassium phosphate, and potassium molybdate are about 2 per cent of the initial conductivities at 35°C. But the temperature coefficients of thorium arsenate and thorium phosphate jellies are considerably less. The graphs obtained by plotting conductivities against temperature are straight lines within the observed range (35°C. to 60°C.). The temperature coefficients of ferric arsenate and aluminum hydroxide sols are also about 2 per cent of the initial conductances. The temperature coefficient of ferric arsenate jelly is less than 2 per cent,— it is only 1 to 1.5 per cent of the conductance at 35°C. For aluminum hydroxide jelly, the temperature coefficient is about 2 per cent.

It has been observed by Dhar and coworkers (9) that the sols of ferric oxide, copper ferrocyanide, Congo red, arsenious trisulfide, silicic acid, etc., show a marked increase in the electric conductivity on aging. Gessner (10) found a decrease in the case of vanadium pentoxide sol. Roy and Dhar (11) observed that in most cases the light effect on colloids is merely an accentuation of the time effect, and consequently, on exposure to light, the conductivity increases. The stability of a sol is due to the stabilizing influence of similarly charged ions. Precipitates as well as sols, when aged, are found to have much less capacity of binding ions by adsorptive forces, so much so, that on aging some of the absorbed ions are set free. These free ions go to account for the increase in the observed conductivity.

The process of gelation is a specific case of coagulation where the uncharged particles instead of settling down after the formation of conglomerates, imbibe the dispersion medium. The coagulant adsorbs some of the ions from the free electrolytes of the medium, and consequently the total conductivity of a jelly system is a little less than the additive conductivities of the components, as has been found in the cases of aluminum hydroxide, ferric arsenate, and thorium molybdate jellies. When thorium nitrate is mixed with potassium molybdate to form the jelly, the reaction appears to proceed as follows:

$$Th(NO_3)_4 + 2K_2MoO_4 = Th(MoO_4)_2 + 4KNO_3$$

During the reaction, thorium molybdate comes down as a gelatinous mass, and thus some of the thorium and molybdate ions are removed from the field. In order to form the colloidal phase of thorium molybdate, some of the stabilizing ions are further adsorbed from the system. This accounts for the 25 per cent diminution in the conductance with respect to the additive values of the components in the case of thorium molybdate jelly.

The conductivities of thorium arsenate and thorium phosphate show a reverse effect. The conductivity of the jelly is much greater than the conductivities of the jelly-forming components taken together. This is due to the fact that while the normal potassium molybdate, K_2MoO_4, was used for the formation of molybdate jellies, the dihydrogen salts, KH_2AsO_4 and KH_2PO_4, were employed in the case of arsenate or phosphate jellies, where the reaction may be assumed to take place as follows:

$$Th(NO_3)_4 + 2KH_2AsO_4 = Th(HAsO_4)_2 + 2KNO_3 + 2HNO_3$$

From this reaction, it is clear that, owing to the formation of nitric acid, more ions are available after the reaction and consequently, in spite of the diminution due to the usual reasons, there is an increase in the conductivity of the system.

Though the conductivity of sols has been investigated by many workers, the temperature influence appears to have been neglected. The influence of temperature on the conductances of simple salts, according to Kohlrausch's classical expression, is linear within a sufficiently wide range and the temperature coefficients per degree approximate to about 2 per cent. The rise in the conductivity on the increase of the temperature is due to an increase in the mobility of the ions. The temperature coefficients of the jellies show an interesting feature. It appears that the increase in mobility of ions in jellies with rise of temperature is somewhat less than in the case of sols or solutions, and therefore the temperature coefficients are less than 2 per cent of the initial in the jellies. This point is exhibited in the case of thorium arsenate, thorium phosphate, and ferric arsenate jellies.

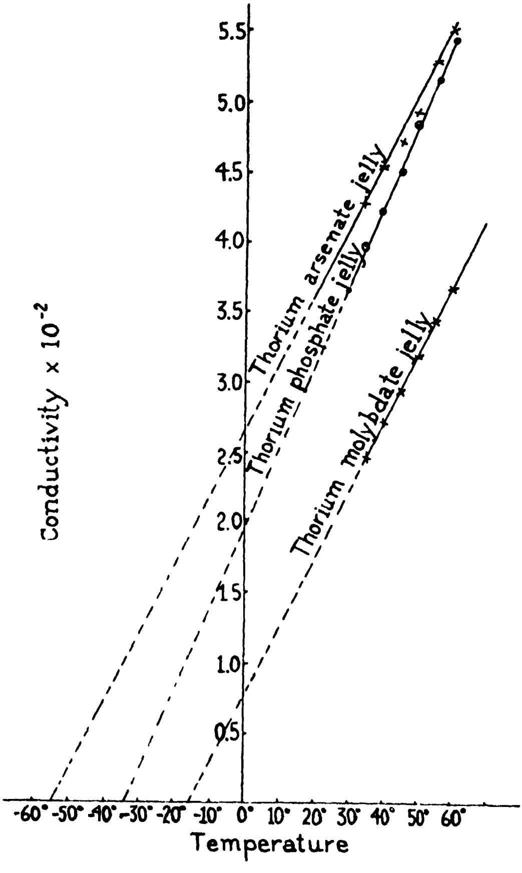

FIG. 1. THE INFLUENCE OF TEMPERATURE ON THE CONDUCTIVITY OF THORIUM JELLIES

One thing interesting to note is the deviation from the usual parallelism between temperature coefficients of conductance and the viscosity of the solvent medium. Ordinarily, it has been found that the conductivity of solutions becomes zero at temperatures near about −39°C. The jellies which we have investigated would have zero conductance at the temperatures given in table 8, as found by extrapolation (the relation between conductivity and temperature has been supposed to be linear down to the zero conductance).

The temperature at which water is supposed to possess an infinite viscosity is −34°C., a temperature at which it has almost no conductivity. When a sol undergoes setting, it gradually begins to gain in viscosity, and finally, it loses all its fluidity. From this, we might have expected a gradual decrease in conductivity too during the course of jelly formation,—a fact contrary to the observations. It shows that the decrease in the fluidity with the fall of temperature is materially very much different from the decrease during the course of jelly formation. It is an interesting fact that the water bound in a jelly offers no resistance to the ions present in the system.

TABLE 8

Temperatures of zero conductance of jellies

JELLY	TEMPERATURE OF ZERO CONDUCTANCE
	degrees C.
Thorium arsenate	−56
Thorium phosphate	−34
Thorium molybdate	−15
Ferric arsenate	−25
Aluminum hydroxide	−20

The conductivities of the jellies so far studied are mainly due to the electrolytic impurities, and in their comparison the effect of actual colloidal micelles is negligible. It is impossible to get an inorganic jelly without the free ions in the system, and as such, the conductivity is not a good property to throw much light on the nature of jellies. Laing and McBain got a difference of about one-fourth in conductivities of soap gels and curds. Even our completely opaque jellies, which may be called curds, do not show much marked decrease in the conductivity during the development of opalescence.

SUMMARY

1. The electrical conductivities of jelly-forming systems of thorium arsenate, thorium phosphate, thorium molybdate, ferric arsenate, and aluminum hydroxide have been investigated

2. It has been shown that once the equilibrium has been established between the jelly-forming components, the electrical conductivity becomes constant and no change is observed during the course of jelly formation or after the setting of the jelly. There is a slight decrease in the conductivity of thorium arsenate along with the development of opalescence until the jelly becomes completely opaque.

3. When the jellies are allowed to age for a number of days, the conductivity increases in all the cases.

4. The conductivities of thorium arsenate and thorium phosphate jellies are greater than the additive values for the conductivities of their components, because in their preparation the dihydrogen salts were used, which give rise to free nitric acid. In the case of thorium molybdate jelly, where a normal salt was used, the conductivity was less than that of the components. This is also the case with aluminum hydroxide.

5. The temperature influence on the conductivity of the jellies has also been investigated between 35°C. and 60°C. The relation between temperature and conductivity has been found to be linear within a wide range. The temperatures of zero conductance have been extrapolated.

6. The temperature coefficient for thorium molybdate and aluminum hydroxide jellies is about 2 per cent of the original at 35°C., while in the other cases, it is markedly less than 2 per cent (about 1 to 1.5 per cent).

The author expresses his indebtedness to Professor N. R. Dhar for his kind interest.

REFERENCES

(1) LAING AND MCBAIN: J. Chem. Soc. **117**, 1506 (1920).

(2) PRAKASH, S., AND DHAR, N. R.: J. Indian Chem. Soc. **6**, 391 (1929); Kolloid-Z. **60**, 184 (1932).

(3) PRAKASH, S., AND DHAR, N. R . J. Indian Chem. Soc. **7**, 417 (1930).

(4) PRAKASH, S., AND BISWAS, N. N.: J. Indian Chem. Soc. **8**, 549 (1931).

(5) PRAKASH, S.: J. Phys. Chem. **36**, 2483 (1932).

(6) PRAKASH, S.: Z. anorg. allgem. Chem. **201**, 301 (1931); **208**, 163 (1932).

(7) PRAKASH AND DHAR: J. Indian Chem. Soc. **6**, 587 (1929).

(8) HOLMES, H. N., AND ARNOLD, R.: J. Am. Chem. Soc. **40**, 1014 (1918).

(9) DHAR AND COWORKERS: Kolloid-Z. **42**, 120 (1927); Z. anorg. Chem. **168**, 209 (1927).

(10) GESSNER: Kolloidchem. Beihefte **19**, 283 (1924).

(11) ROY AND DHAR: J. Phys. Chem. **34**, 122 (1930).

PROMOTER ACTION IN THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS. IV[1,2]

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INTRODUCTION

The previous papers in this series (1, 2, 3) gave data for the decomposition of sodium hypochlorite in the presence of hydrated copper oxide, the catalyst, and also data for the decomposition of the hypochlorite when the catalyst was mixed with certain other catalytically inert oxides which have been designated as promoters (4). In the third paper of the series (3) the author pointed out that the promoter seemed to be effective in the formation and preservation of the active centers on the surface of the catalyst particles. It was also suggested that an ideally promoted catalyst is one in which each molecule of catalyst is separated from its neighbors in a definite way by a fixed number of molecules of promoter, possibly arranged in a definite pattern. This paper gives additional data showing the promoter effect of certain oxides and other insoluble substances on the catalytic decomposition of hypochlorite and in addition shows that there is no apparent simple relation between the crystal structure of the promoters and their activity.

EXPERIMENTAL

Materials and apparatus

The hypochlorite, catalyst, and promoters were prepared as described previously (3). A shaker apparatus, similar to the one originally designed by Walton, was used in following the reaction (5).

Experimental procedure

The procedure followed in these experiments was essentially the same as that outlined in previous papers. However, the details were modified somewhat in those cases where it was necessary to precipitate the catalyst

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[1] Contribution No. 40 from the Chemical Laboratory of the University of Utah.

[2] Part of the experimental results presented in this paper were reported to the Chemical Division of the American Association for the Advancement of Science at the Pasadena Meeting, June, 1931.

as oxide and the promoter as sulfate, carbonate, or other insoluble substance. For example, when it was desired to study the promoter effect of barium sulfate in the presence of the catalyst, barium and copper ions were introduced into the reaction flask and then at the proper time a solution containing the hypochlorite and the sulfate ions was introduced through the side-neck of the flask. This procedure insured the coprecipitation of the two insoluble substances.

RESULTS

In the experiments recorded in this paper the substances designated as "promoters" (when used in the absence of the catalyst) had no effect on the velocity of the reaction. Not only did the authors avoid using mixed catalysts for this study but they also selected a catalyst of moderate activity. In this way the promoter effect of the catalytically inert substances was more apparent.

TABLE 1

*Velocity of the reaction as related to the ratio of promoter atoms added to one atom of catalyst**

CADMIUM AS CdO		CALCIUM AS CaO		MERCURY AS HgO	
Ratio	$K \times 10^4$	Ratio	$K \times 10^4$	Ratio	$K \times 10^4$
0.00	10	0.00	10	0.00	10
0.07	30	0.10	14	0.70	48
0.14	132	0.265	35	1.4	80
0.208	205	0.35	40	2.1	108
0.278	192	0.52	46	2.8	176
0.348	171	0.70	43	3.48	126
0.417	142	0.87	40	4.15	112
0.70	100	1.30	33	5.55	87
1.04	55	1.72	26	7.1	60
1.72	42	2.61	14		

* Hydrated copper oxide is the catalyst in all cases.

The results are summarized in tables 1 to 3 and shown graphically in figures 1 and 2. The rate of the reactions is expressed by means of the unimolecular constant ($K \times 10^4$) and by giving the volume of oxygen liberated at various time intervals.

DISCUSSION OF RESULTS

The data given in table 1 and presented graphically in figure 1 show the effect of increasing amounts of promoters on the rate of the catalyzed reaction. Further, they show that the maximum promotion is obtained, not at a definite ratio of promoter to catalyst atoms, but rather at various ratios, depending upon the promoter used. With each promoter studied, it is apparent that its effect becomes negligible as the ratio of promoter to catalyst becomes high. This may be explained, as suggested in the previous paper, by assuming that the active centers of the catalyst are covered at the higher ratios. On the other hand, the fact that maximum promotion comes at various ratios of catalyst to promoter seems to indicate that the promoter effect is due to a physical spreading out of the catalyst (perhaps on a foundation of promoter molecules), rather than to any definite arrangement (crystal pattern) of catalyst and promoter as was suggested in the third paper of the series.

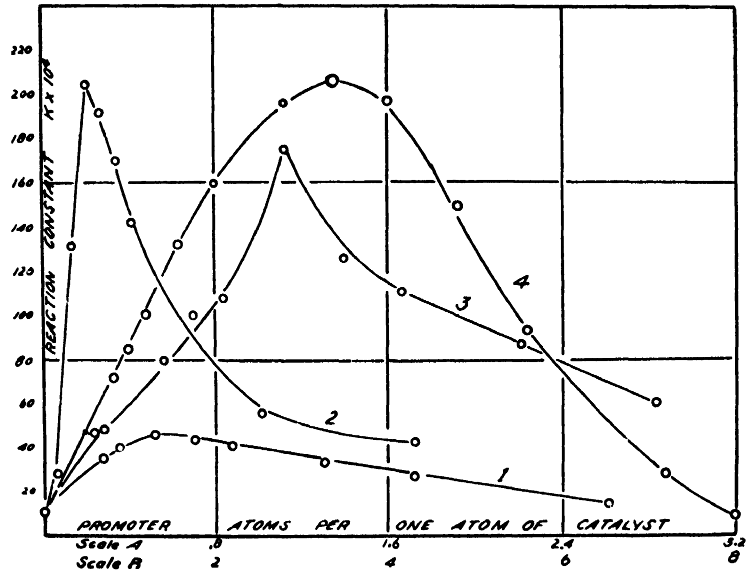

FIG. 1. CURVES SHOWING THE PROMOTER EFFECT OF VARIOUS OXIDES ON THE COPPER OXIDE CATALYSIS OF HYPOCHLORITE SOLUTION

Curves 1 and 2 are plotted to scale A. Curves 3 and 4 are plotted to scale B.

Curve 1, calcium oxide; curve 2, cadmium oxide; curve 3, mercuric oxide; curve 4, magnesium oxide. Data for curve 4 were taken from the third paper of this series.

Additional data which point in the same direction are given in tables 2 and 3 and shown graphically in figure 2. It will be observed that there is no apparent simple relationship between the crystal structure of the promoter and its activity. It appears that many insoluble substances can serve as a promoter if coprecipitation of the catalyst and promoter is attained (see numbers 7 and 8 in table 2).

That the mechanical spreading of a catalyst by an inactive substance results in a "promoter effect" seems to be clearly shown by the above data.

TABLE 2

Promoter action of various insoluble substances on the copper oxide catalysis of sodium hypochlorite solution

NO	RATIO OF CATALYST TO PROMOTER		CUBIC CENTIMETERS OF OXYGEN LIBERATED AT VARIOUS TIME INTERVALS											
	Catalyst	Promoter												
1	CuO	None	Minutes	3	12	20	30	40	50	60	80	100		
			cc. O_2	0.35	0 7	1 0	1 3	1 6	1 9	2 25	2 85	3 42		
2	CuO	BaO	Minutes	3	6	9	12	15	21	24	27	30	35	
	1 to	1 39	cc. O_2	1 45	2 5	3 8	4 4	5 3	6 9	7 6	8 3	8 8	9 7	
3	CuO	BaC_2O_4	Minutes	3	6	9	12	15	18	21	24	27		
	1 to	1 39	cc. O_2	1 6	2 7	3 6	4 6	5 7	6 6	7 7	8 7	9 65		
4	CuO	CaC_2O_4	Minutes	3	6	9	12	15	21	24	30	35	40	50
	1 to	1 78	cc. O_2	1 2	1 8	2 2	2 5	2 8	3 3	3 5	3 9	4 1	4 4	5 0
5	CuO	$BaCO_3$	Minutes	3	6	9	12	18	21	27	35	40	45	50
	1 to	1 39	cc. O_2	2 1	2 4	2 7	2 9	3 3	3 5	3 83	4 35	4 6	4 8	5 1
6	CuO	$CaCO_3$	Minutes	5	10	15	20	25	30	40	50	60	70	85
	1 to	1 78	cc O_2	0 3	0 4	0 5	0 7	0 8	1 0	1 35	1 78	2 3	2 9	4 0
7	CuO*	$BaSO_4$	Minutes	3	6	9	12	18	24	30	40	50	60	
	1 to	1 39	cc. O_2	0 3	0 5	0 6	0 7	0 9	1 05	1 23	1 53	1 83	2 1	
8	CuO†	$BaSO_4$	Minutes	3	6	9	12	18	24	30	40	50	60	
	1 to	1 39	cc. O_2	1 7	2 3	2 6	2 8	3 1	3 45	3 73		4 6		

* The copper oxide and barium sulfate were precipitated separately and then mixed

† The copper oxide and barium sulfate were coprecipitated

TABLE 3

The relationship of crystal structure of certain oxides to their promoter activity in the copper oxide catalysis of hypochlorite*

PROMOTER	$\lambda \times 10^4$ AT MAXIMUM PROMOTION	CRYSTAL SYSTEM	STRUCTURE TYPE
Copper oxide (catalyst)	7	Triclinic	NaCl (distorted)
Magnesium oxide†	207	Cubic	NaCl
Cadmium oxide	205	Cubic	NaCl
Calcium oxide	43	Cubic	NaCl
Barium oxide	75	Cubic	NaCl
Mercuric oxide	176	Orthorhombic	HgO
Ferric oxide‡	99	Hexagonal	Fe_2O_3
Barium sulfate	19	Orthorhombic	$BaSO_4$
Calcium carbonate	20	Orthorhombic	KNO_3
Calcium oxalate	21	No data	
Barium oxalate	76	No data	
Barium chromate	7	No data	

* Crystal structure data were obtained from The Structure of Crystals, by Wyckoff, 2nd edition. The Chemical Catalog Co., New York (1931)

† Data from the third paper of this series.

‡ Data from the second paper of this series.

However it does not seem reasonable to suppose that such large increases in reaction rate produced by such small quantities of promoter can be completely accounted for in this manner. It seems apparent that some other explanation still is to be sought

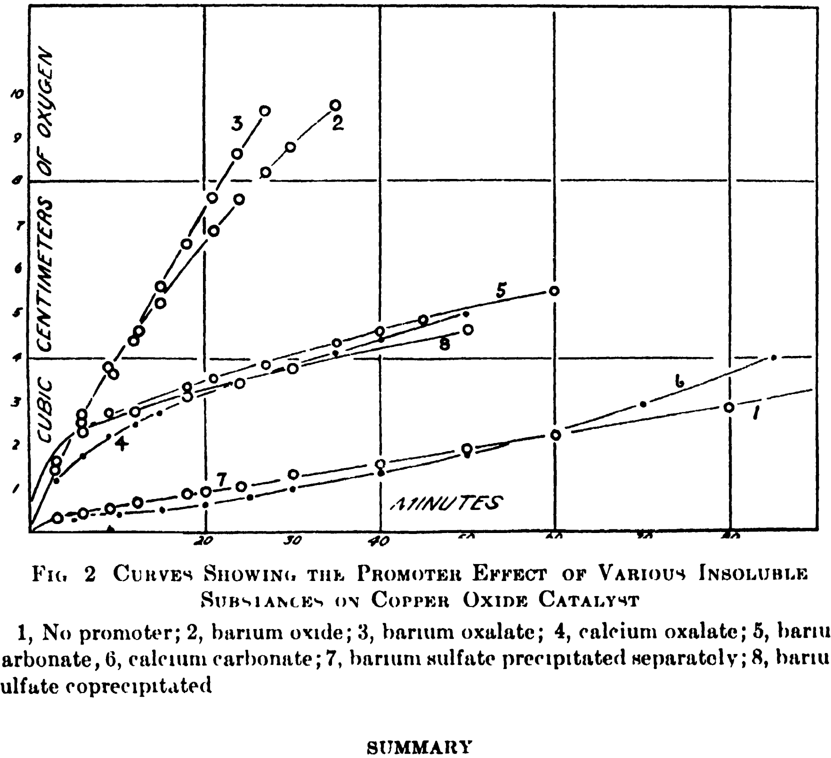

FIG. 2 CURVES SHOWING THE PROMOTER EFFECT OF VARIOUS INSOLUBLE SUBSTANCES ON COPPER OXIDE CATALYST

1, No promoter; 2, barium oxide; 3, barium oxalate; 4, calcium oxalate; 5, barium carbonate, 6, calcium carbonate; 7, barium sulfate precipitated separately; 8, barium sulfate coprecipitated

SUMMARY

1. The promoter effect of several oxides and other insoluble substances has been determined in the copper oxide catalysis of sodium hypochlorite solution.

2. There seems to be no simple relationship between the crystal structure of a promoter and its activity.

3. Promoter action seems to be due in part to a mechanical spreading of the catalyst

REFERENCES

(1) LEWIS. J. Phys. Chem **32,** 243-54 (1928)
(2) LEWIS· J Phys Chem **32,** 1808-18 (1928)
(3) LEWIS· J. Phys. Chem **35,** 915-9 (1931)
(4) RIDEAL AND TAYLOR· Catalysis in Theory and Practice Macmillan and Co, London (1926).
(5) WALTON· Z Physik Chem **47,** 185 (1904)

THE ATOMIC MASS OF SODIUM. II

THE SODIUM CHLORIDE–SILVER RATIO

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The present study of the sodium chloride–silver ratio was designed to develop and test a new general method for the determination of atomic mass ratios.

PURIFICATION OF REAGENTS

The reagents used in this work were purified by methods (1) which were shown to be adequate by suitable tests. The general criterion of acceptable purity for any reagent was that the amount used in a single analytical system or 1500 g. of standard solution would introduce no silver or chloride impurities equivalent to more than 0.005 mg. of silver. Simple and sensitive nephelometric tests (2) made it possible to fulfill this condition with certainty.

Sodium chloride

The sodium chloride was obtained from 500 g. of Merck's C. P. reagent. It was precipitated successively three times from saturated solution with central fractions of hydrogen chloride distilled from C. P. concentrated hydrochloric acid, fused in platinum, and then crystallized three times from pure water. Before each treatment the solution was filtered through a Munroe crucible, and the recovered cyrstals were always dried in a centrifuge at 1500 r. p. m. for fifteen minutes. Uniform initial and final fractions were rejected in each of the six precipitations or crystallizations. The work was conducted under glass covers to eliminate dust, and the solutions came into contact only with platinum dishes

The 107 g. of material obtained after the sixth crystallization was separated into five fractions by crystallization from water. As each of the fractions was obtained it was redissolved in water and passed through a platinum Munroe crucible directly into a platinum receiver. The solution was evaporated in a 150-cc. platinum dish, and the dry salt was transferred with a spatula to covered platinum cups in a vacuum desiccator. Each of the platinum implements was weighed just before and after handling each fraction. The maximum possible extent and distribution of the platinum impurities was thus determined with precision (see table 1). Since only part of the platinum accidentally scraped from the dish and spatula was transferred with the samples, it is safe to say that the average error due to platinum impurities in the sodium chloride is well below the maximum platinum content of 1 part in 270,000.

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[1] National Research Fellow in Chemistry, 1930–1932.

TABLE 1

Platinum impurities in sodium chloride

FRACTION NO	WEIGHT	MILLIGRAMS OF PLATINUM IMPURITIES FROM			
		150-cc dish	Spatula	Receiver	Filter
	grams				
1	26	0.04	0.00	0.00	0.02
2	26	0.06	0.00	in	in
3	18	0.04	0.00	all	all
4	25	0.07	0.03	five	five
5	12	0.12	0.02		

Neutrality of sodium chloride

It is not possible for well-dried, vacuum-desiccated sodium chloride to hydrolyze to any great extent during fusion. Samples of the sodium chloride fused in air or nitrogen by the method hereinafter described were shown to be neutral in ordinary tests with indicators. The possibility of slight hydrolysis during fusion is now being studied in more detail with the cell: tungsten | tungsten oxide | fused NaCl (satd.) | unfused NaCl (satd.) | tungsten oxide | tungsten.

Containers

The various Pyrex flasks and beakers used in the analyses were all examined for cracks by the sensitive phenolphthalein–sodium hydroxide test. This was an important precaution, since almost invisible cracks were found in several cases. All vessels were cleaned by washing in order with soap and water, cleaning solution, concentrated aqua ammonia, nitric acid, and water. It was noticed that the removal of silver chloride from glass vessels with ammonia leaves on the walls a film of some material containing an excess of silver over chloride. This observation has a bearing on many points of technique in nephelometric work with silver chloride.

THE ANALYSES

The analytical weighings and transfers of material were made with precautions which make them accurate to about 0.01 mg. For each weighing the air density was determined from temperature, pressure, and psychrometric observations, and vacuum corrections were applied on the basis of the known volumes of the weights and densities of the materials. Weighings were made by the method of substitution, on a No. 10 Troemner balance sensitive to 0.01 mg. with a load of 20 g. It may be noted that 0.01 mg. of silver, silver chloride, sodium chloride, or the equivalent in suitably diluted solutions, is distinctly visible; it is possible to be reasonably certain that carefully controlled weighings and transfers are quantitative to this extent. In the few cases in which larger quantities of the materials may be present in invisible films, the procedures insure the same degree of certainty.

Titration analyses

For each analysis a 5.4 to 5.5 g. sample of sodium chloride was fused in a weighed 20-cc. platinum crucible in an electric furnace, after desiccation in vacuum over fused potassium hydroxide for at least three days. The covered crucible was completely inclosed in a covered quartz crucible surrounded by a quartz muffle. The crucible and contents were raised to 810°C. over about twenty minutes, then held at 810° to 860°C. for five to thirty minutes. After the loaded crucible had cooled sufficiently, it was returned to a desiccator, and cooled completely before weighing.

By the use of a suitable counterpoise crucible, the weights of the empty or charged crucible could be duplicated to 0.01 mg. in successive weighings, made at widely separated times. In no case was there any evidence of gain of moisture from air of low or moderate humidity in which all weighings were made. The weighed crucible containing the fused salt was placed in a Pyrex beaker with a "dripless" lip, and the salt was dissolved in 500 cc. of pure water. The resulting solution was transferred to the analytical system without delay.

The thoroughly washed crucible was dried in a porcelain electric furnace at 300°C., and the rechecked difference between the weights of the crucible and counterpoise served as the initial value in the next analysis. The volatility and solubility of the platinum crucible under these conditions was very small. In nine analyses the crucible used in fusing the sodium chloride lost only 0.07 mg., which was distributed as a uniform steady loss. A quartz crucible was used for the sample which was fused in nitrogen carrying a small amount of hydrogen chloride.

The purified silver, in the form of fused buttons and electrolytic crystals, was prepared for weighing by heating to 500°C. in an evacuated quartz tube, and was kept in a desiccator over fused potassium hydroxide. The silver was weighed directly on the balance pan, and handled with ivory-tipped forceps and a watch glass. Successive weighings of the same silver, involving transfer to the watch glass and return to the pan, could be duplicated to 0.01 mg. A satisfactory check consisted in making the substitutions in the order: weights-silver-weights. For each analysis silver approximately 1.8454 times the predetermined weight of the sodium chloride was taken for exact weighing. Crystals made up only 2 to 8 mg. of the total weight of silver. The silver was dissolved in 1:1 nitric acid, using 76.0 cc. of 7.57 molar nitric acid per 10.00 g. of silver, with precautions to avoid mechanical loss. The solution was diluted to 500 cc. before transferring it to the analytical system, at room temperature.

The general scheme of analysis, designed to obtain evidence on several points of interest, is shown in table 2. In each case one of the 500 cc. solutions was added to the other at the rate of 4 cc. per minute. The latter solution was contained in a weighed 3-liter glass-stoppered Pyrex Erlenmeyer flask, which was rotated repeatedly during the addition. The transfer apparatus consisted of a 250-cc. tall-form funnel with a stirring rod ground into the top of the stem and slotted to permit the drop by drop addition of solution to the large flask. The rod extended beyond the flared rim of the funnel, and was bent to form an obtuse angle a little above the rim. It could be removed to permit the rapid addition of wash water. The transfers were made under glass covers to avoid dust impurities.

TABLE 2

Scheme of analysis

$NaCl$ ADDED TO $AgNO_3$				$AgNO_3$ ADDED TO $NaCl$			
Fraction No	Fused in	Time fused	Maximum temperature	Fraction No	Fused in	Time fused	Maximum temperature
		minutes	*degrees C*			*minutes*	*degrees C*
1a	Air	20	830	1b	Air	5	820
2a	N_2	30	830	2b	N_2	30	830
3a	Air	5	820	3b	HCl N_2	15	860
4a	Air	10	820	4b	Air	10	810
5a	Air	10	810	5b	Air	5	810

After addition of the wash waters, the system was made up with water, by weighing on a large balance, to contain 1520.7 g. of solution per 10.0000 g. of silver (7.8796 g. of sodium nitrate). Each supernatant analytical solution thus had the same composition as the solutions used in previous work (3) on the end point of the sodium chloride–silver titration. The analytical system was brought to equilibrium at 0°C. and portions of the supernatant liquid were withdrawn and filtered at this temperature, and later analyzed in the manner described in detail in the above-mentioned report, by nephelometric comparison (at room temperature) with exactly similar standard solutions containing measured amounts of silver and chloride. A number of these standards, each containing 7.8796 g. of sodium nitrate and 28.46 g. of hydrogen nitrate per 1520.7 g. of solution, were made up to cover a short range of silver and chloride concentrations in the end point region. This range could be narrowed as desired, either by weighing out the original samples of sodium chloride and silver in more nearly equivalent amounts, or by making additions as described below, and also by allowing ample time for the complete coagulation of the colloidal silver chloride in the analytical systems.

After preliminary analyses of the supernatant analytical liquid, its silver and chloride contents were adjusted to approximate equality in the usual manner, by the addition of dilute standard silver nitrate or sodium chloride solutions. The end point of the titration was then determined by four to eight sets of nephelometric analyses made over a period of several days with two or three independently prepared standards The average difference in the measured silver and chloride concentrations located the end point directly, with an uncertainty equivalent to only about 0.02 mg. of silver. In several cases further adjustments were made, and the end point determinations were repeated. It may be noted that *when the liquids were near the correct end point*, small measured additions of silver nitrate or sodium chloride agreed quantitatively with the resulting changes shown in the composition of the supernatant liquids by the standard solution tests, within about 0.02 mg. of silver or its chloride equivalent.

In the analyses of samples 2b, 4a, and 4b, the end point was also determined by potentiometric analyses made at 0°C. with the cells:

Ag | AgCl | Analytical solution | Standard solution | AgCl | Ag
Ag | Analytical solution | Standard solution | Ag

In these measurements, in order to eliminate errors due to liquid junction potentials, it was necessary to make slight adjustments in the nitric acid concentration of the analytical solutions. Exact predetermination of the nitric acid concentration was prevented by the small variations in the amount of nitrogen oxides retained during solution of the silver. This point presented no difficulty, as the necessary adjustments could be made with precision after titration of test portions of the solutions with standard alkali.

The differences in the silver and chloride concentrations in each of the supernatant liquids, as found in the potentiometric analyses, gave the same end points as the corresponding nephelometric analyses. The solubility values found were uniformly a little lower for the potentiometric experiments. It seems likely that identical results would be obtained in both cases by allowing ample time for the complete coagulation of the colloidal silver chloride. For the sake of uniformity the solubility values given in subsequent tables are the nephelometric values, which must be preferred in estimating silver and chloride in rejected liquors and washings.

Gravimetric analyses

A new technique for the collection and estimation of silver chloride was also studied. In developing this gravimetric procedure, every effort was made to minimize or eliminate minor corrections, in recognition of the fact that a multiplicity of corrections increases rather than diminishes constant errors.

At the completion of each titration analysis the supernatant liquid remaining was poured into a weighed 600-cc. beaker, then decanted through an accurately weighed Munroe crucible while still at about 0°C. The bulk of the precipitate was transferred to the beaker with the last of the liquid. The flask was inverted in a ring over the beaker and the last visible traces of silver chloride were removed with the aid of a wash-bottle with an S-shaped nozzle, filled with a portion of the cold, filtered, supernatant liquid. The crystals in the beaker were drained, and the filtered supernatant liquid was collected and later analyzed for silver and chloride by comparison with standard solutions having the same composition, in the nephelometer. The liquid retained by the silver chloride was estimated by weighing the beaker and its contents to the nearest 0.5 g.

The silver chloride was washed with ten 25-cc. portions of dilute acid containing in all 1.0 cc. of 7.57 molar nitric acid, then with four 25-cc. portions of pure water, with the last of which it was transferred to the Munroe crucible. A perforated platinum plate was used to shield the filter mat. The silver chloride was dried at a temperature increased from 80° to 110°C. during four hours, in a porcelain electric furnace, then heated at 300°C. for twelve hours before weighing. The crucible and contents were again heated at 300°C. for six hours and weighed a second time. In ten experiments the loss during the second heating averaged 0.014 mg., and never exceeded 0.03 mg. Satisfactory proof of the constancy in weight of the Munroe crucible during these operations was obtained by removing the bulk of the precipitate, dissolving any adhering silver chloride in aqua ammonia, and washing in proper sequence with water and nitric acid, before drying and reweighing the crucible. Under these conditions the difference in weight between the crucible and counterpoise could be rechecked to about 0.02 mg. When such rechecks are desired, the crucible should not be inverted during washing, as loose particles sometimes develop on the top of the mat.

No "loss on fusion correction" for the silver chloride was made. Hönigschmid and Chan (4) have shown that the loss on fusion after drying silver chloride at 300°C. is so small as to be of doubtful significance.

The nitric acid–water washings of the silver chloride were preserved and later made to 500 cc. with the aqua ammonia–nitric acid–water washings. The latter washings consisted of 50.0 cc. of 1.5 molar ammonium hydroxide prepared by distilling concentrated C. P. aqua ammonia into water in a Pyrex apparatus, 25.0 cc. of 7.57 molar nitric acid, and water, used in proper sequence. Care was taken not to acidify the ammonia solution before the final combination of washings. These washings covered all surfaces which might have retained silver chloride, in the following vessels: (1) the pipette and filter used in withdrawing and filtering the nephelometric test portions, (2) the containers used for storing the washings, (3) the transfer beaker and stirring rod, (4) the receiving flask, (5) the 3-liter analysis flask, and (6) the porcelain interior of the electric furnace.

The silver and chloride in the combined washings were estimated by nephelometric comparison of 20.0-cc. test portions with equal volumes of standard solutions. The standard solutions were made up in 500 cc. amounts, each containing 26.0 cc. of 7.57 molar nitric acid, 50.0 cc. of 1.5 molar ammonium hydroxide, solution to correspond to the weighed supernatant liquid retained by the silver chloride, and measured equivalent amounts of silver and chloride. The nitric acid and ammonia solutions were equal aliquot portions of the same reagents used in the washings; the other solution was a quantity of one of the standard solutions used in the end point tests, corrected for its silver and chloride content. These standards thus had precisely the same composition as the combined washings, as the silver and chloride content could be adjusted to the desired value after one approximation. Under the conditions described above, analyses made in duplicate or triplicate agreed within 0.02 mg. It should be emphasized that it is only by such systematic regulation of conditions that the anomalies usually observed in these tests may be eliminated.

Analyses of solutions

In recognition of the possibility that abnormalities due to adsorption effects might be revealed thereby, all of the various supernatant liquids and washings from the precipitated silver chloride were analyzed both for their silver and chloride contents. Each of the values given in the summary of these analyses (table 3) is the mean of at least three measurements made by the standard solution method. On the average the individual values may be trusted to about 0.02 mg. The chloride concentrations in the table are multiplied by the factor Ag/Cl. Compared with normal solubility values, most of the values given in the first two columns of the table are a little too high. It would have been impractical to wait for the complete coagulation of the colloidal silver chloride in these experiments, although it was recognized that this would slightly increase the precision of the end point measurements. The single low value represents a solution frozen, melted, and analyzed while held at 0°C., under conditions preventing it from attaining compiete saturation.

TABLE 3

Summary of analyses of solutions

SAMPLE NO	SOLUTION NEAR END POINT, 0°C.		SAME AFTER SEPARATION		COMBINED WASHINGS	
	Chloride	Silver	Chloride	Silver	Chloride	Silver
	mg /liter	*mg /liter*	*mg /liter*	*mg /liter*	*mg /500 ml*	*mg /500 ml.*
1a	0.56	0.50	0.80	0.76	0.99	1.00
1b	0.73	0.66	0.78	0.97	0.44	0.43
2a	0.69	0.69	0.77	0.76	0.37	0.37
2b	0.73	0.67	0.79	0.74	0.40	0.40
3a	0.73	0.71	0.79	0.75	0.40	0.40
3b	0.71	0.70	0.72	0.74	0.51	0.51
4a	0.65	0.71	0.72	0.78	0.33	0.33
4b	0.71	0.70	0.95	0.91	0.48	0.49
5a	0.66	0.61	0.77	0.82	0.48	0.44
5b	0.75	0.68	0.86	0.76	0.37	0.39

DISCUSSION OF RESULTS

The present research was designed for the development and testing of new procedures for use in the determination of atomic mass ratios, and attention is confined mainly to this aspect of the experimental results.

Titration analyses

The pairs of analyses made with uniform samples of fractions 1, 2, 4, and 5 give values for the sodium chloride–silver ratio which show that the new analytical method is an unusually *precise* one. The average deviation of the individual ratios from the respective means is only 3 parts in 540,000. There is no discrepancy between the known precision of the separate steps of the analytical procedure and the experimentally observed precision of the entire procedure. Such a discrepancy might have been expected if the silver or sodium chloride was not uniform, or if the composition of the silver chloride precipitates with respect to silver and chloride was not definite.

The results obtained for fraction 3 were excluded from the above considerations by the predetermined analytical scheme. The analysis of sample 3b shows that some of the hydrogen chloride dissolved in the molten sodium chloride was not removed when the material was cooled in a current of nitrogen. Other portions of the sodium chloride, fused under the same conditions as sample 3b, but not analyzed, gave an acid reaction with indicators when dissolved in water. The high sodium chloride–silver ratio obtained for sample 3a is puzzling. The only reason to believe that the result does not represent a correct analysis of the fraction is to be found in the analyses of the adjacent fractions.

It was recognized that any impurities in the sodium chloride obtained in the sixth crystallization would tend to concentrate in fraction 5, and that the analyses of this fraction could have no standing as determinations of the sodium chloride-silver ratio. However, these analyses accomplish their main purpose by showing that even the residual liquor from which the other fractions were crystallized was remarkably pure.

TABLE 4

Summary of analyses

NO	NaCl IN VACUUM	Ag IN VACUUM	NET Ag ADDED	FINAL Ag EXCESS	TOTAL Ag ≎ NaCl	RATIO NaCl Ag
	grams	*grams*	*mg*	*mg*	*grams*	
1a	5 48994	10 13092	1 45	−0 09	10 13246	0 541817
1b	5 43976	10 03832	1 70	−0 11	10 03981*	0 541819
2a	5 48976	10 13054	1 69	±0 00	10 13223	0 541812
2b	5 47090	10 09582	1 33	−0 09	10 09724	0 541821
3a	5 42144	10 00451	0 48	−0 03	10 00502	0 541872
3b	5 4360	10 0314	2 54	−0 02	10 0340	(0 54176)
4a	5 59192	10 31920	1 53	+0 09	10 32064	0 541819
4b	5 43087	10 02204	1 46	−0 02	10 02352	0 541813
5a	5 51668	10 17998	2 22	−0 08	10 18218*	(0 541798)
5b	5 42755	10 01596	1 71	−0 11	10 01778	(0 541792)

NO	DRY AgCl IN VACUUM†	AgCl IN ALL SUPERNATANT LIQUIDS	AgCl IN COMBINED WASHINGS	TOTAL UNFUSED AgCl	RATIO AgCl Ag
	grams	*mg*	*mg*	*grams*	
1a	13 45877	1 56	(1 32)	13 46165	(1 32857)
1b	13 33790	1 44	0 59	13 33993	1 32870
2a	13 46031	1 51	0 49	13 46231	1 32866
2b	13 41347	1 52	0 53	13 41552	1 32863
3a	13 29126	1 48	0 53	13 29327	1 32866
3b	13 3286	1 44	0 68	13 3307	1 3286
4a	13 71081	1 38	0 44	13 71263	1 32866
4b	13 31536	1 63	0 64	13 31763	1 32864
5a	13 52674	1 45	0 64	13 52883	1 32868
5b	13 30805	1 63	0 49	13 31017	1 32866

* Corrected as noted in text

† Corrected for minute amounts of sodium chloride added in adjusting the solutions to the end point

In discussing the *accuracy* of the new method, it is important to consider the evidence concerning the composition of precipitated silver chloride, which is the only factor in this type of precipitation analysis over which the analyst has no direct control. At other points the methods available for checking the accuracy of the procedures and the purity of the materials are adequate. For the titration method, the problem here involved is considerably simplified by the fact that it is only the silver nitrate or sodium chloride adsorbed or otherwise included by the precipitate that need be considered. Moreover, if adsorption or occlusion is an important factor in determining the composition of the precipitate, silver chloride coagulated in a solution containing excess of sodium chloride and that formed in excess of silver nitrate should differ markedly, and the difference might be expected to appear in the measured sodium chloride–silver ratios. In the present experiments, the results obtained by reversal of the order of precipitation, in pairs of analyses in which uniform samples of sodium chloride and silver were used, indicate that no such adsorption or occlusion occurred. Further evidence to support this conclusion is found in the fact that the removal of successive layers from the precipitates by warming and washing showed no anomalies, when the end point adjustments were properly made.

The above remarks apply only to experiments in which the silver chloride was in contact with solutions extremely close to the correct end point. In other cases, with either silver nitrate or sodium chloride in excess, some of the excess material may be taken up by the precipitate. It follows that under certain conditions, depending on the manner in which the end point is approached, the silver and chloride content of the supernatant liquid cannot be trusted to show the difference in the amounts of silver and chloride in the system.

An example of such a case is found in the analytical data for sample 1b. The change in the silver content of the supernatant liquid indicates that silver was in excess in the precipitate during the end point determination, and that it was later ejected by the precipitate. The ejection must have occurred either during the warming which accompanied the separation of the supernatant liquid or in the period of standing which preceded the separation. Proper correction was made for the excess silver found in the 1220 cc. of separated liquid. Reference to the measured ratios shows that the silver chloride expelled the excess silver to return to the same composition as other precipitates which were never in contact with a solution containing excess silver. This behavior offers additional evidence of the definite composition of the original silver chloride precipitates. It also indicates that adsorbed or occluded material is not held very firmly, an observation which would appear to explain the absence of irregularities due to reversal of the titration for the pairs of samples. It may be noted that the analysis of sample 1b was the first to be completed; in subsequent analyses the adjustments to the end point were made in a manner calculated to avoid the difficulty.

Gravimetric analyses

The silver chloride–silver ratios found in the gravimetric analyses show in a general way that the silver and sodium chloride used in this work were highly pure. It may also be inferred that the amount of sodium nitrate retained by the precipitates was extremely small. The value obtained for sample 1a is open to suspicion for the reason that the combined washings were found to be saturated at room temperature, after acidification. It is highly probable that some silver chloride was lost at this stage. This accident emphasizes the importance of not overloading the aqua ammonia washings, rather than any serious weakness in the procedures. In fact, except for their "incidental" feature the new procedures were satisfactory in every respect, and under more favorable conditions, in "direct" gravimetric analyses, should be capable of even higher precision.

In conclusion, the significance of the present results as a determination of the atomic mass of sodium may be briefly noted. Seven of the titration analyses have been made with carefully purified reagents and materials, by a method in which it has not been possible to detect any constant errors greater than the known accidental errors of the analytical procedures. In deriving a value for the NaCl:Ag ratio from these seven experiments, convention requires the rejection of the abnormally high value, whereupon the remaining six give 0.541817 ± 0.0000010 for the ratio. Thus, if $Cl = 35.457$ and $Ag = 107.880$, the atomic mass of sodium is 22.994. Seven gravimetric analyses were made with sodium chloride containing no known impurities, but only five of these are properly eligible for use in estimating the NaCl: AgCl ratio. These five analyses yield the value 0.40779 ± 0.0000026, whence $Na \doteq 22.994$.

Thanks are due to Professor George A. Hulett for many suggestions which have been found helpful in the present series of experiments.

REFERENCES

(1) Scott, A. F., and Johnson, C. R.: J. Phys Chem. **33**, 1978 (1929).
(2) Johnson, C R.: J. Phys. Chem. **36**, 1944 (1932).
(3) Johnson, C. R.: J. Phys. Chem. **36**, 1942 (1932)
(4) Honigschmid, O., Chan, S B., and Birckenbach, L : Z. anorg. allgem. Chem. **163**, 315 (1927).

THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE IN PROTEIN SYSTEMS[1]

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While the effect of salts upon the solubility of proteins has been studied by Mellanby (1), Sörensen (2), Cohn (3), Stadie (4), Florkin (5), Green (6), and others, the effect of proteins upon the solubility of salts has been little studied. Pauli and Stenzinger (7) have measured the solubility of calcium sulfate in various protein solutions. Failey (8) has studied the effect of edestin nitrate on the solubility of thallous chloride. These workers, however, have merely correlated the change in solubility of the salt with the protein concentration. In the present investigation this change has been related to the ionic strength of the solution as calculated under certain assumptions. Adair (9) determined the activity coefficients of chloride ion in edestin chloride solutions equilibrated with hydrochloric acid and correlated them with the charge on the protein in a manner similar to that developed in this paper.

PREPARATION OF MATERIALS

Egg albumin

This protein was prepared from the whites of strictly fresh eggs according to the method of Sörensen (2). The crystals obtained were dissolved and recrystallized three times from ammonium sulfate solution. The final material, placed in cellophane sacs, was dialyzed against running tap water for forty-eight hours, against distilled water for four days, and finally freed from electrolytes by means of electrodialysis. The approximately 5 per cent stock solution resulting left a negligible ash and was completely free of chlorides (see table 1). It had a pH of 4.75 and a conductivity of 7.6×10^{-5} mhos.

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[2] The material for this paper is from a dissertation submitted by Gilbert C. H. Stone to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Edestin

Crystals of the protein were prepared by a modification of the Osborne method (10). Finely ground hemp seed was extracted with a 10 per cent sodium chloride solution. The resulting liquid, diluted with three times its volume of water at 50°C. and allowed to cool, deposited crystals of edestin. The protein was recrystallized five times from a 10 per cent sodium chloride solution and three times from a 7.5 per cent sodium nitrate solution by means of dilution. The resulting crystals were repeatedly suspended in water and centrifuged until free from electrolytes (see table 1). By placing the protein in water in a volumetric flask and adding a slight excess of 0.1 *N* sodium hydroxide a solution was obtained. The amount of alkali added was noted. The liquid was made up to volume and used as a stock solution.

TABLE 1

Analysis of protein preparations

SUBSTANCE	CHLORIDE ANALYSIS				ASH ANALYSIS
	N/10 hydrochloric acid added	Protein added (approximate)	Nitric acid added	Silver chloride obtained	Ash per gram of protein
	ml	*grams*	*ml*	*grams*	*mg*
	0.00	20	100	0.0002	
	20.00	0	0	0.2866	
	20.00	0	100	0.2867	
	20.00	0	100	0.2866	
Egg albumin	20.00	15	100	0.2866	2.19
	20.00	10	100	0.2865	2.71
Edestin	20.00	15	100	0.2868	0.0
	20.00	10	100	0.2867	0.1
Excelsin	20.00	15	100	0.2868	0.0
	20.00	10	100	0.2866	0.1
Hemoglobin	20.00	15	100	0.2864	5.42*
	20.00	10	100	0.2867	5.45*

* The amount of ash due to iron is given variously as 4.8–6.7 mg. per gram of hemoglobin.

Excelsin

This protein was also prepared by a modification of the Osborne method (11). The oil contained in a meal of finely ground Brazil nuts was expressed. The resulting solids were extracted with a 10 per cent sodium nitrate solution, and the protein recovered from this liquid by the addition of anhydrous sodium sulfate to 22 per cent by weight at a temperature of 37°C. According to Howe (12) this procedure completely precipitates globulins. The resulting precipitate was ground with 20 per cent sodium nitrate to dissolve it and the solution diluted with ten times its volume of water. A white amorphous precipitate settled out. The solid was three times dissolved in 20 per cent sodium nitrate and precipitated by dilution. The white amorphous material was finally dissolved in a minimum of 20 per cent sodium nitrate solution, placed in cellophane sacs, and dialyzed against running tap water for three days and against distilled water for three days. The precipitated globulin so obtained was pure white and crystalline. It was washed four times by suspending in water and centrifuging. From the electrolyte-free preparation (see table 1) a stock solution of the globulin was made up in the same manner as that of edestin.

Hemoglobin[3]

This conjugated protein was prepared according to the method of Stadie (13) by electrodialyzing fresh horse cells that had been previously washed four times in physiological saline solution. The crystals obtained, however, as noted also by Burk (14), even after washing with ice-cold distilled water, contained considerable quantities of salt, either bound or free. Therefore the crystals were dissolved in water and the cell debris removed by adding quantities of toluene and centrifuging—the stroma either becoming suspended in the toluene layer or settling to the bottom of the cup. The clear solution was once more electrodialyzed until salt-free (see table 1).

Reduced hemoglobin, used in these investigations, was obtained by evacuating the bottles containing the oxyhemoglobin, passing hydrogen through the solutions, and working with them in an atmosphere of hydrogen. Stock solutions had a pH of 6.75 and a conductivity of 4.8×10^{-5} mhos.

During the preparation of these proteins adequate amounts of C.P. toluene were added as a preservative. The proteins were used immediately after they were prepared, or stored, when necessary, in the ice-box under toluene.

To prepare electrolyte-free egg albumin and hemoglobin for the determination of their molecular weights by means of osmotic pressure measurements, Burk (14) used practically the same procedures as were described above. His values for the molecular weights agreed well with those ob-

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[3] The authors are indebted to Dr. B. Crieley of the Lederle Laboratories for kindly supplying them with fresh horse cells.

tained by means of other methods. This would indicate that electrodialysis of these protein solutions produced no deleterious effects.

Thallous chloride

The saturating salt was Kahlbaum's "zur Analyse" thallous chloride, recrystallized twice from distilled water and twice from conductivity water.

Sodium hydroxide

The 1.0 *N* alkali was made from a saturated chloride-free, carbon dioxide-free solution of Kahlbaum's sodium hydroxide from metallic sodium, by dilution with carbon dioxide-free water.

EXPERIMENTAL

The solubility of thallous chloride in water was determined as follows. Approximately 10 g. of saturating salt was suspended in 200 ml. of conductivity water in each of six glass-stoppered Pyrex bottles, and rotated for twenty-four hours in a water thermostat at a temperature of 25.00 ± 0.01°C. The salt was allowed to settle in the bottles in the thermostat and the saturated solutions filtered through cotton by means of a pressure syphon into glass-stoppered flasks. Samples of the solution were weighed out and chlorides determined gravimetrically as silver chloride.

An average of eighteen determinations involving three equilibrations gave the solubility of thallous chloride in water as 0.01612 ± 0.00003 moles per 1000 g. of water. This value checks with that of Bray and Winninghoff (15). In four of the determinations the solvent was saturated with toluene. No change in solubility resulted. The toluene with which the protein solutions were saturated, therefore, is a negligible factor.

In determining the solubility of thallous chloride in the protein solutions the same method of equilibrating and filtering was used, the solvent, however, being the protein solution. These solutions were made up by determining the per cent of protein in the stock solutions either by the Kjeldahl or the dry weight method. These gave concordant results. The nitrogen factors taken are as follows: Egg albumin 15.56 (16), edestin 18.69 (10), excelsin 18.30 (11), hemoglobin 16.86.

The solutions were then made up by weight from the stock solutions and the calculated amount of 1.0 *N* sodium hydroxide added.

A sample was removed for the determination of its pH.

The bottles containing the thallous chloride were washed three times with distilled water, then once with the appropriate protein solution before equilibrating.

The following procedure for determining chlorides in the protein solutions gave a maximum error of 0.3 per cent on solutions of known chloride content (see table 1). To weighed samples of the solution of approximately 100 g. a 50 per cent excess of silver nitrate dissolved in concentrated nitric acid was added. One hundred ml. of concentrated, chloride-free nitric acid was added to the solution and a few drops of caprylic alcohol to prevent foaming. The beakers were covered with watch glasses and digested overnight on a hot plate. The protein entirely destroyed by the nitric acid left the silver chloride coagulated and easily filterable. The solutions were allowed to cool to room temperature; the precipitate was washed thoroughly by decantation, filtered, and weighed.

TABLE 2

Effect of time on the solubility of thallous chloride in an excelsin solution at 25°C

PROTEIN CONCENTRATION PER KILOGRAM OF WATER	TIME OF EQUILIBRATION	MOLALITY OF THALLOUS CHLORIDE
grams	*hours*	
35.52	24	0.01984
35.52	72	0.01985
35.52	120	0.01985
35.52	168	0.01985

TABLE 3

Activity coefficients of thallous chloride in isoelectric, electrolyte-free protein solutions

PROTEIN	CONCENTRATION OF PROTEIN IN GRAMS PER KILOGRAM OF WATER	MOLALITY OF THALLOUS CHLORIDE	$-\log \gamma \pm$ TlCl
Egg albumin	5.61	0.01622	0.0730
	11.13	0.01624	0.0736
	19.31	0.01640	0.0780
	29.63	0.01646	0.0793
	39.14	0.01647	0.0796
	47.49	0.01667	0.0850
Hemoglobin	10.79	0.01620	0.0724
	15.16	0.01631	0.0755
	22.77	0.01638	0.0773
	26.85	0.01648	0.0800
	31.03	0.01657	0.0824

The hydrogen-ion concentration of the solutions was determined at 25°C. by means of a Clark rocking electrode. Tenth normal hydrochloric acid was the reference standard, its pH being assumed to be 1.08. The hydrogen used was purified by passing it over copper at 650–700°C.

The densities of the solutions were measured by means of a Westphal balance at 25.0 ± 0.5°C.

In order to determine the time necessary for equilibrium to be attained

TABLE 4

Activity coefficients of thallous chloride in protein solutions of varying "ionic strengths"

PROTEIN	GRAMS OF PROTEIN PER KILOGRAM OF WATER	pH OF PROTEIN SOLUTIONS	C_{OH^-} OF SOLUTIONS $\times 10^3$	MOLALITY OF THALLOUS CHLORIDE	$-\log \gamma_\pm$	$\sqrt{\mu}$	$\sqrt{\mu_s}$
Egg albumin	1 228	12 25	25 00	0 01793	0 1168	0 230	0 275
	2 455	12 23	25 00	0 01808	0 1203	0 239	0 299
	4 910	12 19	25 00	0 01837	0 1272	0 246	0 317
	10 05	12 00	25 00	0 01959	0 1550	0 319	0 477
	20 11	11 76	25 00	0 02051	0 1750	0 333	0 511
	30 16	11 44	25 00	0 02064	0 1778	0 338	0 526
	40 22	11 02	25 00	0 02039	0 1724	0 329	0 511
	50 27	10 43	25 00	0 02002	0 1645	0 312	0 418
	20 00	5 03	1 00	0 01648	0 0799	0 131	0.132
	20 00	5 50	2 50	0 01663	0 0839	0 139	0 151
	20 00	6 34	5 00	0 01693	0 0917	0 162	0 201
	20 00	10 64	10 00	0 01805	0 1195	0 219	0 314
	20 00	11 78	25 00	0 02041	0 1729	0 331	0 507
	20 00	12 31	50 00	0 02204	0 2063	0 378	0 552
Edestin	5 001	12 22	25 00	0 01818	0 1226	0 229	0 497
	10 002	12 16	25 00	0 01855	0 1313	0 240	0 599
	20 00	12 01	25 00	0 01920	0 1464	0 264	0 786
	30 01	11 84	25 00	0 01957	0 1545	0 282	0 916
	40 01	11 62	25 00	0 01974	0 1584	0 290	0 980
	50 01	11 38	25 00	0 01954	0 1540	0 290	0 994
	4 536	12 80	100 00	0 02104	0 1860	0 316	0 490
	13 61	12 77	100 00	0 02163	0 1990	0 368	0 678
	24 95	12 72	100 00	0 02222	0 2098	0 403	1 018
	45 36	12 63	100 00	0 02353	0 2347	0 434	1 272
	20 00	11 21	10 00	0 01745	0 1047	0 202	0 595
	20 00	11 81	20 00	0 01861	0 1327	0.261	0 836
	20 00	12 11	30 00	0 01944	0 1517	0 286	0 877
	20 00	12 27	40 00	0 01993	0 1626	0 317	0 973
	20 00	12 40	50 00	0 02047	0 1741	0 331	0 962
Excelsin	3 058	12 24	25 00	0 01805	0 1195	0 223	0 439
	6 115	12 21	25 00	0 01812	0 1211	0 231	0 517
	9 173	12 16	25 00	0 01835	0 1266	0 243	0 622
	18 35	12 03	25 00	0 01902	0 1422	0 265	0 795
	36 69	11 62	25 00	0 01979	0 1594	0 298	1 023
	55 04	11 16	25 00	0 01952	0 1536	0 290	1 004
	20 00	10 43	5 00	0 01714	0 0971	0 160	0 133
	20 00	11 25	10 00	0 01730	0 1009	0 200	0 345
	20 00	11 84	20 00	0 01866	0 1340	0 254	0 627
	20 00	12 14	30 00	0 01922	0 1468	0 272	0 619
	20 00	12 30	40 00	0 01975	0 1587	0 297	0 704
	20 00	12 43	50 00	0 02013	0 1669	0 305	0.606

TABLE 4—*Concluded*

PROTEIN	GRAMS OF PROTEIN PER KILOGRAM OF WATER	pH OF PROTEIN SOLUTIONS	C_{OH^-} OF SOLUTIONS $\times 10^3$	MOLALITY OF THALLOUS CHLORIDE	$-\log\gamma_\pm$	$\sqrt{\mu}$	$\sqrt{\mu_s}$
Hemoglobin	2 949	12 22	25 00	0 01777	0 1126	0 257	0 236
	5 529	12 12	25 00	0 01801	0 1185	0 314	0 273
	7 372	12 09	25 00	0 01771	0 1113	0 320	0 276
	10 30	12 01	25 00	0 01834	0 1264	0 331	0 686
	20 60	11 58	25 00	0 01943	0 1514	0 373	0 813
	30 90	11 10	25 00	0 02003	0 1648	0 360	0 781
	41 20	10 70	25 00	0 02014	0 1671	0 333	0 709
	51 50	10 35	25 00	0 02009	0 1660	0 310	0 646
	20 00	6 96	0 50	0 01647	0 0796	0 131	0 144
	20 00	6 84	0 10	0 01692	0 0915	0 130	0 135
	20 00	6 67	0 05	0 01651	0 0808	0 128	0 127
	20 00	7 28	1 00	0 01581	0 0618	0 128	0 133
	20 00	7 81	2 50	0 01602	0 0675	0 137	0 166
	20 00	8 65	5 00	0 01645	0 0792	0 160	0 246
	20 00	10 41	10 00	0 01752	0 1065	0 220	0 423
	20 00	11 52	25 00	0 01939	0 1506	0 252	0 461
	20 00	12 28	50 00	0 02005	0 1652	0 438	0 925

between the saturating salt and the solvent, and also to determine whether the solubility of the thallous chloride in the protein solutions varied with time owing to the action of the alkali on the protein, a time curve was made. Excelsin was dissolved in a solution of sodium hydroxide so that the alkali was 0.025 molal and the protein concentration 35.52 g. per 1000 g. of water. This solution was equilibrated in the usual manner with the thallous chloride crystals. Samples were removed and analyzed at the end of one, three, five, and seven days. The results are tabulated in table 2. It can be seen that the solubility of the thallous chloride is constant over the period of a week's equilibration, and that twenty-four hours of rotating the solution with the saturating salt is sufficient for equilibrium.

DISCUSSION

Tables 3 and 4 summarize the data and results of these experiments. The first table gives the negative logarithm of the activity coefficient of thallous chloride in the presence of isoelectric, electrolyte-free protein, calculated according to the equation (17)

$$-\log\gamma_\pm = \log\frac{1}{m^0_\pm} - \log\frac{1}{m_\pm} \qquad (1)$$

$\log\frac{1}{m^0_\pm}$ being taken as 1.8630 (18).

Figure 1 is a plot of the data in table 3 and some of that in table 4 with $-\log \gamma_{\pm}$ as ordinates and grams of protein per 1000 g. of water as abscissae. The lowest curve represents the effect of varying concentrations of isoelectric protein, without the addition of alkali, upon the negative logarithm of the activity coefficient of thallous chloride. The points fall on a straight line, the slope of which is quite small. Isoelectric, electrolyte-free protein, even in high concentrations, does not greatly effect the solubility of the saturating salt. If the decrease in the activity coefficient of the saturating salt be due to interionic effects, then isoelectric protein might be expected not to raise the solubility at all. However, at their isoelectric points proteins, on the basis of the zwitter ion theory, have a high total charge in spite of the fact that their net charge is zero—the number of positive and negative charges on the molecule being equal. In addition there probably exist a few molecules having a small net positive or negative charge which would be expected to cause a rise in the curve.

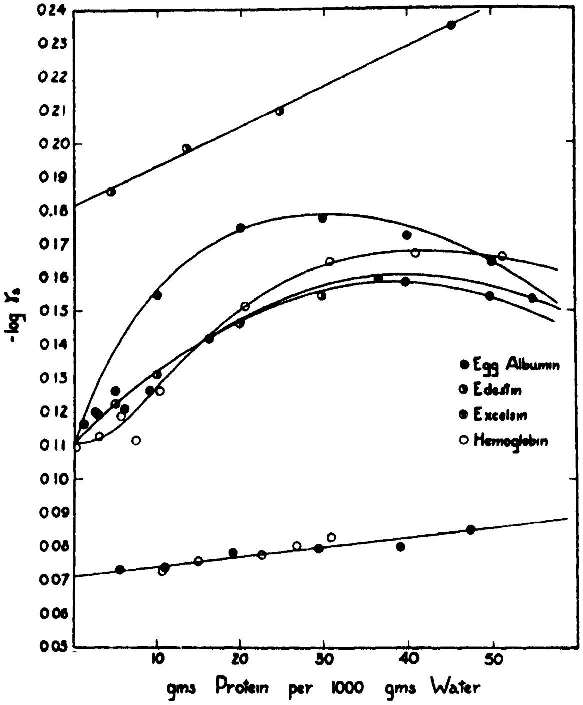

FIG. 1. EFFECT ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE OF VARYING CONCENTRATIONS OF ISOELECTRIC, ELECTROLYTE-FREE PROTEIN SOLUTIONS, OF PROTEIN SOLUTIONS IN 0.025 N SODIUM HYDROXIDE, AND OF PROTEIN SOLUTIONS IN 0.1 N SODIUM HYDROXIDE

If base is added to an isoelectric protein solution, the molecules of the ampholyte acquire a net negative charge. Their effect on the activity coefficient of an ion may now be a function not only of the protein concentration but also of the charge on each individual protein molecule. As a first assumption one might expect the charged protein molecules to affect the activity coefficient of electrolytes as if they were contributing to the ionic strength an amount equal to the product of the square of their valence by their molality. Then in dilute solutions one should find, according to Debye (19),

$$- \log \gamma_{\pm} = 0.505 \sqrt{\mu} \qquad (2)$$

The number of hydroxyl ions bound in a protein solution is obtainable from pH measurements. The protein concentration being known, the protein molality and its contribution to the "ionic strength" may be calculated if a value be assumed for the molecular weight of the protein.

The points on the curve in the middle portion of the graph (figure 1) represent the effect of varying concentrations of protein in 0.025 N sodium hydroxide upon the negative logarithm of the activity coefficient of thallous chloride. It may be seen that the rise is at first linear with increasing protein concentration. Soon the curve slopes off and a maximum is reached after which $-\log \gamma_{\pm}$ falls with higher concentrations of ampholyte.

When high protein concentrations are employed, there is insufficient sodium hydroxide present to convert the molecules into their most basic sodium salt. These molecules, binding less base, do not raise the ionic strength of the solution as much as protein molecules at their maximum binding capacity. For this reason, as the protein concentration increases the ionic strength increases to a maximum. Then, beyond the point where it has combined with all the base present, the curve falls off. Further addition of protein serves to decrease the ionic strength. This phenomenon will again be noted when $-\log \gamma_{\pm}$ is plotted against $\sqrt{\mu}$.

In the case of hemoglobin, the curve does not rise linearly at first. This protein does not seem to behave like the others, as has been noted throughout the investigation. These abnormalities and the importance of hemoglobin biologically indicate that this protein merits further study.

The uppermost curve represents the effect of varying concentrations of edestin in 0.1 N sodium hydroxide upon $-\log \gamma_{\pm}$. Here a linear relationship exists, at least up to a protein concentration of 5 per cent. In this case there is sufficient alkali to satisfy the maximum binding capacity of the highest concentrations of edestin used. An increase of protein concentration in such alkaline solutions produces an increase in the ionic strength of the solution and a corresponding rise of $-\log \gamma_{\pm}$.

Figure 2 is a graph of the data in table 3, with $-\log \gamma_{\pm}$ as ordinates and $\sqrt{\mu}$, (on the basis of the molecular weights of the proteins as determined by Svedberg) as abscissae. Points were obtained for constant protein (2 per cent) and varying alkali concentrations, and also varying protein and constant amounts (0.025 N) of sodium hydroxide.

It will be noted that the points fall approximately on the straight dotted lines in the case of egg albumin, edestin, and excelsin. Hemoglobin seems to be at variance with this linear relationship.

However, according to equation 2 the slope of these lines should be 0.505, at least in the solutions of lowest ionic strength. A broken line of such slope is drawn on the graph. All the observed values fall below the

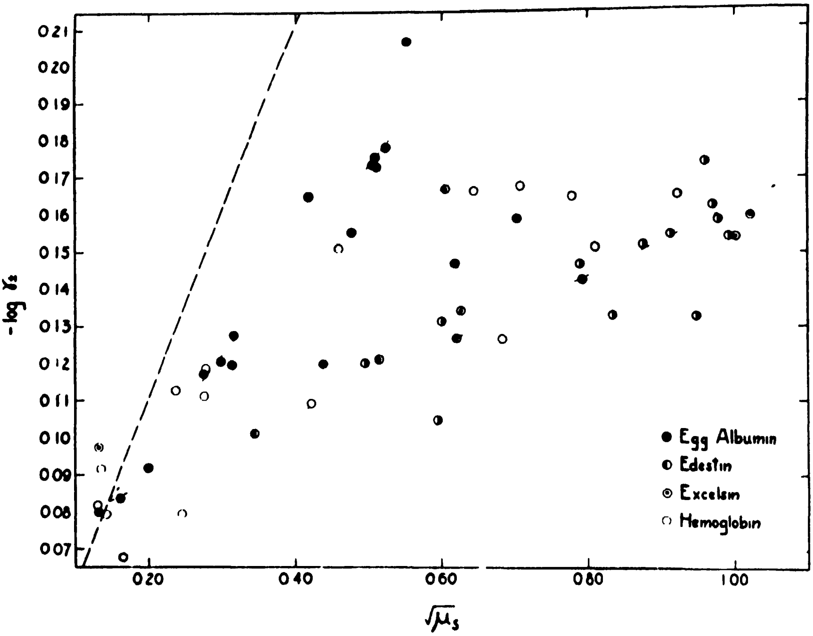

FIG. 2. INFLUENCE OF THE "IONIC STRENGTH" OF PROTEIN SOLUTIONS, CALCULATED ON THE BASIS OF SVEDBERG'S MOLECULAR WEIGHTS, ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE

theoretical. The ionic strengths were therefore recalculated, varying the apparent molecular weight, in order to obtain the theoretical slope. It was found that if an apparent molecular weight of 11,400 be assigned to each of the proteins, the ionic strength calculated on that basis would give points which lie on the same straight line having a slope of 0.505.

Table 4 gives these calculations and may require further explanation as to the method and theory involved. The molality has been computed by dividing the concentration of the protein, given in grams per 1000 g. of water, by the apparent molecular weight of 11,400. This value was assumed to be the same for all the proteins. Column 3 gives the pH as determined electrometrically. The concentration of hydroxyl ions was calculated from the pH on the basis that

$$aH^+ \times aOH^- = aH_2O = 10^{-14} \text{ at } 25°C. \tag{3}$$

$$aH^+ \times [OH^-]\,\gamma_{OH} = 10^{-14} \tag{4}$$

$$-\log [OH^-] = 14 - pH + \log \gamma_{OH^-} \tag{5}$$

Since the activity coefficients of all uni-univalent electrolytes have approximately the same value at low ionic strengths, it was believed justifiable to assume γ_{OH^-} equal to $\gamma_{\pm TlCl}$.

Knowing the amount of hydroxyl ion added to the protein in the form of sodium hydroxide, and knowing the calculated value of the hydroxyl ion concentration of the solution after the addition of alkali, a simple subtraction gives the base bound by the protein. The apparent valence is the concentration of base bound divided by the molality of the protein, or the base bound per molecule of protein. These figures are not whole numbers, but rather an average valence. Owing to the complex structure of the proteins and the many dissociable hydrogen ions, at any instant not all the molecules may bear the same number of charges. It is rather the time average of the net charge that is important, giving an average valence.

TABLE 5

Densities of protein solutions at 25° C.

PER CENT PROTEIN	EGG ALBUMIN	EDESTIN	EXCELSIN	HEMOGLOBIN
0.5	0.9993	0.9992	0.9991	0.9992
1.0	1.0012	1.0012	1.0011	1.0012
1.5	1.0030	1.0030	1.0031	1.0030
2.0	1.0045	1.0048	1.0050	1.0046
2.5	1.0058	1.0064	1.0067	1.0060
3.0	1.0070	1.0079	1.0083	1.0073
3.5	1.0080	1.0092	1.0097	1.0084
4.0	1.0090	1.0105	1.0110	1.0094
4.5	1.0098	1.0117	1.0122	1.0103
5.0	1.0105	1.0128	1.0134	1.0112

From these data the "ionic strength" of the protein solutions may be calculated, which, when added to the ionic strength due to the residual sodium and hydroxyl ions and the dissolved thallous chloride, gives the total ionic strength of the solutions. This quantity changed from a weight to a volume basis by the aid of the table of densities (table 5) is given in column 7, since μ in equation 2 is calculated from molarities, not from molalities.

Values of $\sqrt{\mu}$, tabulated in column 8 were calculated in a precisely similar manner employing the particle size or molecular weights of Svedberg, measured by the ultracentrifuge method. Egg albumin was taken as 34,500 (20), hemoglobin as 68,000 (21), and edestin and excelsin as 212,000 (22, 23). It is these values that were used in the graph, figure 2.

In figure 3 the square roots of the ionic strengths as calculated in column 7 are plotted as abscissae and the values of $-\log \gamma_{\pm}$, column 6, as ordinates.

Egg albumin, excelsin, and edestin conform very well to the straight line curve of slope 0.505. The hemoglobin points, however, scatter around the line. Several different preparations were used. All showed the same effect.

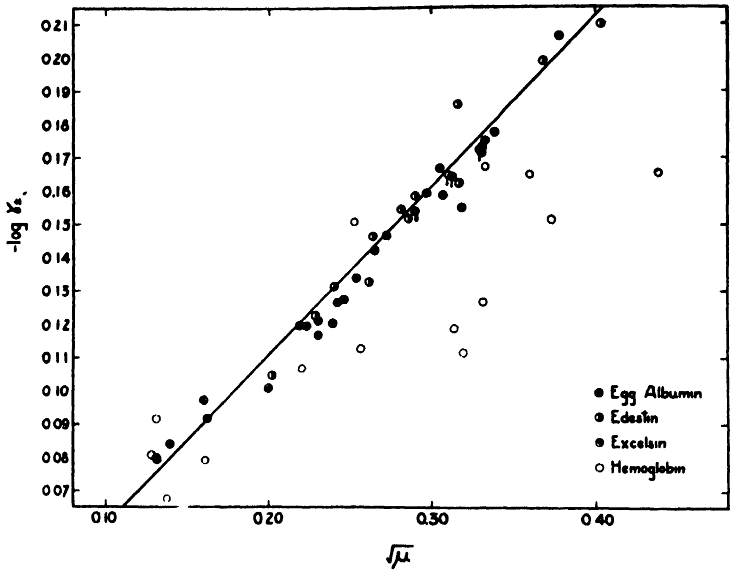

FIG. 3. INFLUENCE OF THE "IONIC STRENGTH" OF PROTEIN SOLUTIONS, CALCULATED ON THE BASIS OF AN ASSUMED MOLECULAR WEIGHT OF 11,400, ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE

The points with arrows are those where the protein concentration is high; the ionic strength having reached a maximum the points have fallen back on the line below the maximum.

The fact that the negative logarithm of the activity coefficient is a linear function of the square root of the ionic strength calculated as above would indicate that sodium proteinates behave similarly to typical electrolytes. This is true even though the apparent valence of the protein be as high as 15, giving good accordance with the Debye limiting law up to ionic strengths as high as 0.18 when the molecular weight of 11,400 is assumed for each protein. However, this should be regarded as an interesting empirical generalization rather than as an indication that there really exist units of weight 11,400 and of high valence which behave in so simple a manner. The uniformity of action indicates an underlying similarity in the interaction between electrolytes and proteins of widely different character.

Perhaps the theory of polyvalent protein ions and their effect on the thermodynamic environment should consider the spacing of charges in addition to the net valence calculated on the basis of molecule size.

It must be noted that some solutions were quite alkaline—the pH rising from the isoelectric point as high as 12.5. At high pH values there might be a disaggregation of the protein into smaller units. Svedberg (23) noted this phenomenon while determining the molecular weights of edestin and excelsin. Near the isoelectric point the weight was 212,000 ± 4,000 but above the pH of 10.5 the molecules broke down into units having a weight of 34,500; he suggests that proteins are built up of these units (24). The "apparent molecular weight" found in the present investigation is 11,400, one-third of the unit 34,500.

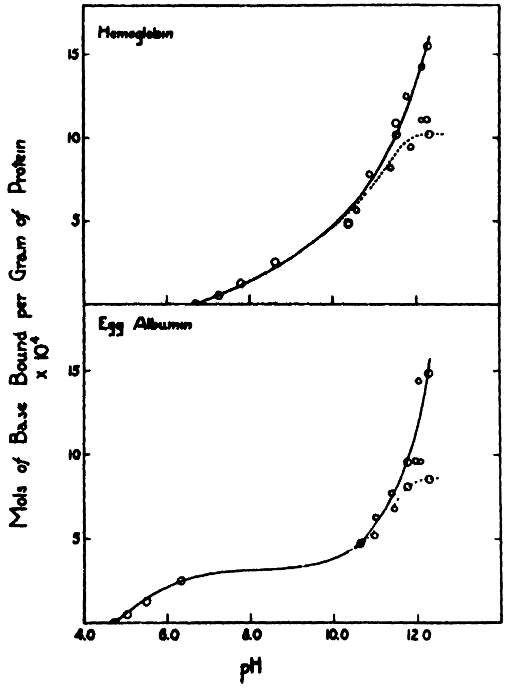

FIG. 4. CORRECTED AND UNCORRECTED TITRATION CURVES OF HEMOGLOBIN AND EGG ALBUMIN

In spite of the fact that the pH values cover a wide range over which, according to the above, a progressive disaggregation should occur, there is, except in the case of hemoglobin, no deviation from a linear relation between $-\log \gamma_{\pm}$ and $\sqrt{\mu}$ exceeding the experimental error.

Figure 4 is a plot of the titration curves of egg albumin and hemoglobin. The base bound per gram of protein is plotted as ordinates; the pH as abscissae. The data was taken from table 4.

When the base bound is calculated in the usual manner by subtracting the concentration of hydroxyl ions of the solution from the concentration added as sodium hydroxide, the [OH⁻] being obtained by the relationship,

$$-\log [\mathrm{OH}^-] = 14 - \mathrm{pH} \qquad (6)$$

the curves obtained are shown in solid lines and compare well with those found in the literature.

However, the concentration of hydroxyl ions must be corrected by means of the activity coefficient (equation 5). Then the base bound will at high pH values be found to differ considerably from that calculated by the first method. The titration curves obtained from such data are given on the graph by means of a dotted line. It can be seen that these corrected curves coincide with the uncorrected up to pH 10. At higher pH values the corrected curve falls lower to the extent of 20 per cent from the uncorrected. This correction factor of the activity coefficient is therefore necessary in order to obtain the true shape of a titration curve.

SUMMARY

1. The activity coefficient of thallous chloride in protein solutions was determined by means of solubility measurements.

2. In isoelectric, electrolyte-free protein solutions the change in solubility of the saturating salt was small, showing that such protein solutions exert little effect. The negative logarithm of the activity coefficient increased linearly with protein concentration.

3. The negative logarithm of the activity coefficient of thallous chloride was found not to be a linear function of the protein concentration in solutions of constant alkali content. A point of maximum solubility was obtained beyond which the solubility decreased in solutions of increasing protein concentration.

4. With solutions of varying protein content and constant alkali concentration, and varying alkali and constant protein concentrations, the negative logarithm of the activity coefficient of thallous chloride rose approximately linearly with increase in the square root of the ionic strength of the solution, calculated in accordance with certain assumptions.

5. If the apparent molecular weight of all the proteins be assumed to be 11,400, all points fell, except in the case of hemoglobin, on the same straight line of theoretical slope 0.505 when $-\log \gamma_{\pm}$ was plotted against $\sqrt{\mu}$.

6. A correction for titration curves was introduced.

REFERENCES

(1) Mellanby, J J Physiol **33**, 338 (1905–06)

(2) Sorensen, S P L Compt rend lab Carlsberg **12**, 1 (1915)
Sorensen, S P L, and Sorensen, M Biochem Z **258**, 16 (1933)

(3) Cohn, E J J Gen Physiol **4**, 697 (1922)
Cohn, E J, and Hendry, J L J Gen Physiol **5**, 521 (1923)
Cohn, E J, and Prentiss, A M J Gen Physiol **8**, 619 (1927)

(4) Stadie, W C J Biol Chem **77**, 241 (1928)

(5) Florkin, M J Biol Chem **87**, 629 (1930)

(6) Green, A A J Biol Chem **93**, 495, 517 (1931), **95**, 47 (1932)

(7) Pauli, W, and Stenzinger, T Biochem Z **205**, 71 (1929)

(8) Failey, C F J Am Chem Soc **54**, 2367 (1932)

(9) Adair, G S Proc Roy Soc London **A120**, 573 (1928)

(10) Osborne, T B J Am Chem Soc **24**, 39 (1902)

(11) Osborne T B J Am Chem Soc **25**, 323 (1903)

(12) Howe, P E J Biol Chem **49**, 93 (1921)

(13) Stadie, W C, and Ross, E C J Biol Chem **68**, 229 (1926)

(14) Burk, N F, and Greenberg, D M J Biol Chem **87**, 197 (1930)

(15) Bray, W C, and Winninghoff, W H J Am Chem Soc **33**, 1663 (1911)

(16) Sorensen, S P L Compt rend lab Carlsberg **18**, 5 (1930)

(17) Lewis and Randall Thermodynamics and the Free Energy of Chemical Substances, p 371 McGraw-Hill Book Co, New York (1923)

(18) International Critical Tables, Vol VII, p 319 McGraw-Hill Book Co, New York (1930)

(19) Debye, P, and Hückel, E Physik Z **24**, 185 (1923)

(20) Svedberg, T and Nichols, J B J Am Chem Soc **48**, 3081 (1926)

(21) Svedberg, T and Nichols, J B J Am Chem Soc **49**, 2920 (1927)

(22) Svedberg, T, and Stamm, A J J Am Chem Soc **51**, 2170 (1929)

(23) Svedberg, T, and Sjogren B J Am Chem Soc **52**, 279 (1930)

(24) Svedberg, T Trans Faraday Soc **26**, 740 (1930)

A CRITICAL STUDY OF SOME IRON-RICH IRON-SILICON ALLOYS

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On account of the technical importance of the iron–silicon alloys, considerable work has been done in recent years (1) on the constitution diagram of the system. Of particular importance both from the standpoint of the purity of the alloys used and the thoroughness of the investigation, is the work of Haughton and Becker, while the earlier work of Phragmen is also noteworthy. It appears that only the compound FeSi is accepted beyond dispute, while there is some doubt regarding the compounds Fe_3Si_2 and $FeSi_2$ (or Fe_2Si_5). The existence of a compound corresponding to Fe_3Si has been advanced by Corson; and Stoughton and Greiner, in their critical review of the literature and from their resistance study, also support Corson's view. On the other hand, Haughton and Becker, Phragmen, Murakami, and others deny the existence of Fe_3Si. Phragmen claims it to be merely a distinguished point in the series of solid solution, particularly because he found the limit of solubility to be 15.4 per cent silicon, as obtained, however, by extrapolation of the x-ray data.

In all the work done so far, each investigator appeared to be merely preoccupied with the interpretation of his results from a purely physical point of view, neglecting altogether considerations which would have been arrived at from a chemical standpoint. It is the writer's specific purpose to bring certain thermodynamic considerations to bear in the interpretation of his results as well as the results of other investigators. Hence, emphasis in this paper will be on chemical and not physical methods.

The writer has been particularly fortunate to have obtained through the kindness of Mr. K. Marsh of the Engineering Foundation Monograph Series, five samples of extremely pure iron–silicon alloys prepared in the Union Carbon and Carbide Research Laboratories, Inc. Some ordinary commercial iron-silicon alloys were also obtained from the Duriron Co., Dayton, Ohio. The composition of the alloys is given in table 1. It will be seen that the composition of the pure alloys in which the writer is mainly interested lies very close to that of Fe_3Si. The samples were received in the "as cast" condition and so they were annealed at about 900°C. for 150 hours in order to insure real equilibrium.

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TABLE 1

Composition of the iron-silicon alloys

NO	PER CENT SI	PER CENT Si BY ANALYSIS	NO	PER CENT Si	PER CENT Si BY ANALYSIS
1	13 0	12 39	5	17 0	15 56
2	14 0	13 11	6*	5 0	4 92
3	14 5	13 99	7*	25 0	Not analyzed
4	15 0	14 50	8*	32 0	Not analyzed

* Commercial alloy.

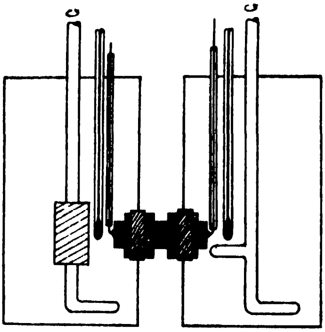

FIG. 1. APPARATUS FOR THE DETERMINATION OF THE THERMOELECTRIC CHARACTERISTICS OF IRON-SILICON ALLOYS

THERMOELECTRIC CHARACTERISTICS

Corson (1) made a study of the change in the resistivity of the iron-silicon alloys with respect to the silicon content, but on account of the fact that he used specimens which were not sufficiently annealed to obtain real equilibrium, doubt has been cast on this phase of his work. It is well known that the true value of the resistance of alloys is very difficult to measure except in the form of a wire, but from a study of Corson's paper the writer is convinced that no systematic error can account for the very sharp cusp at the composition corresponding to Fe_3Si.

As a general rule, the resistance curve is parallel, if not congruent, with the thermoelectric curve, and since the thermoelectric characteristics can be studied much more accurately, the writer adopted this method to ascertain if a similar cusp could be found. As the specimens were only 2 to 6 cm. in length and about 1.5 cm. in radius, a special but simple apparatus had to be constructed as shown in figure 1. The thermal E.M.F. was read against pure nickel at 75°C. and 50°C. at the hot junction and at 0°C. at the cold junction. After considerable trial, we found that by stirring the mushy mixture of pulverized ice in water at a speed of 1500 r.p.m., while the hot water was stirred at a speed of only 500r.p.m., strictly reproducible results could be obtained. The millivoltmeter used was calibrated against a standard cell on the Type K (Leeds and Northrup) potentiometer. The results of this study are shown in figure 2.

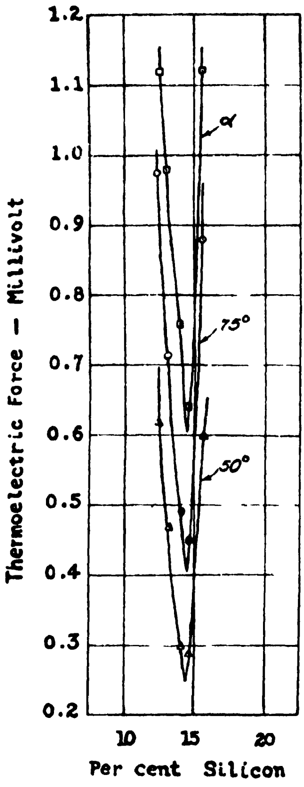

FIG. 2. THE THERMOELECTRIC CHARACTERISTICS OF SOME IRON-SILICON ALLOYS AGAINST NICKEL

The temperature coefficient (α) is also given

The sharp cusp in the resistivity-composition curve obtained by Corson is thus confirmed in figure 2, and since the composition of the alloys used by the writer varied by only small increments, the cusp may be placed with some certainty at exactly 14.35 per cent silicon, corresponding to the compound Fe_3Si. As Corson properly pointed out, the resistivity-composition curve he obtained is characteristic of a binary system of two metallic components forming a continuous series of solid solutions, either or both of which components may also be a truly intermetallic compound. Hence, if the alloy corresponding to the composition of 3Fe/Si were only a distinguished solid solution, the resistivity-composition curve should reasonably be expected merely to vary continuously from the resistivity of pure iron to that of 3Fe/Si without passing through a maximum, as was obtained by Corson. If we consider a truly metallic compound as one that is characterized by low resistivity, then Fe_3Si (hereafter designated as ϕ for convenience) is a metallic compound of the shared electron type, i.e., a nonpolar compound.

THE ELECTRODE POTENTIAL OF IRON-SILICON ALLOYS

The electrode potentials of alloys are very significant characteristics of their condition in the heterogeneous systems, i.e., whether compounds or solid solutions are formed. Suppose we have a cell with pure iron as one electrode and an iron-silicon alloy as the other electrode, both being immersed in the same solution of electrolyte (such as ferrous sulfate); then when a current passes through the cell, a certain quantity of iron is transferred from the pure iron electrode to the alloy electrode, thus

$$\text{Fe(pure)} = \text{Fe(in solid solution)};\ \Delta F = RT \ln a' = -\mathbf{NEF}$$

Hence,

$$\mathbf{E} = -(RT/\mathbf{NF}) \ln a' = -k \ln a' \qquad (1)$$

when the activity of pure iron is taken as unity and a' represents the activity of iron in the solid solution. It is noteworthy that the electrode potential in equation 1 is independent of the nature and concentration of the electrolyte used, provided **N** is the same.

In the case of an intermetallic compound acting as an electrode, the problem becomes much more complicated, as we no longer have an essentially ionic transfer following the Faraday law of electrolysis. This is due to the fact that intermetallic compounds, as a rule, are not of the polar type. The electrode potentials thus obtained may be meaningless, in regard to their thermodynamic significance, being perhaps nothing better than the polarization potentials. Nevertheless, even the polarization potential is also characteristic of the compound and that compound alone, and is, therefore, significant in revealing the presence of a particular compound.

In figure 3 is shown the experimental set-up for the determination of the electrode potential of the iron-silicon alloys against pure iron. The electrolytic hydrogen was first purified in a pyrogallic acid train, then in a platinized asbestos train, heated to about 500°C., and then bubbled through the boiling distilled water in the flask A, the stirring helping to rid the water of any dissolved gases on account of their mutual solubility (i.e., providing a gas–gas interface). After the water had been boiled for thirty to forty-five minutes, a cooling vessel was introduced under the flask. When the water had reached room temperature, the measuring bulb B was evacuated by a pump, and water was allowed to flow in from the reservoir flask A. This operation was repeated, so that the second time we were more certain that the bulb B contained only gas-free water. The requisite amount of the $FeSO_4 \cdot 7H_2O$ salt to make a $N/10$ solution was placed in the cell chamber C and the electrodes introduced as shown in figure 3. The cell chamber was then evacuated and hydrogen allowed to flow in. Stopcocks Nos. 2 and 3 were then opened, so that the flowing hydrogen could force the water from the measuring bulb B into the cell chamber C. During the course of the run, hydrogen was bubbled through the solution at the rate of a bubble per second. The potential was measured on a Type K potentiometer.

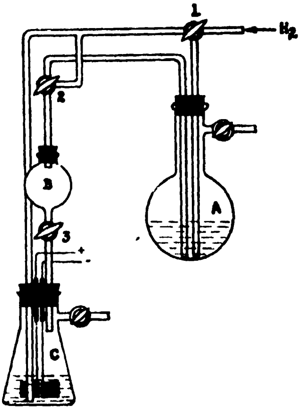

Fig. 3. Apparatus for the Determination of the Electrode Potential of Iron-Silicon Alloys against Pure Iron

The electrolytic iron electrode was kindly prepared for the writer by Mr. T. S. Fuller of the General Electric Research Laboratory. It had been previously remelted twice under very high vacuum. The ends of the electrodes were polished in the same manner as for metallographic examination. It was found that without proper etching, the cell did not come to equilibrium for as long as two weeks. After many trials, it was finally decided to use the ordinary $HF–HNO_3$–glycerine etchant as well as aqua regia. The latter drastic treatment was found necessary in order to remove the effect of cold-working during the process of polishing. In order to remove any surface inequalities due to preferential dissolution, all alloys were again repolished lightly and etched with a weaker solution of $HF–HNO_3$–glycerine. The electrodes, with the exception of the polished surface, were given a smooth coating of paraffin.

A few words may be said regarding the process of recrystallization of the $FeSO_4 \cdot 7H_2O$ salt, as it is very difficult to keep in a reduced state. In the preliminary part of the work, considerable trouble with oxidation of the ferrous salt solution was encountered, but when the recrystallized salt was later used, the trouble disappeared altogether. Baker's ordinary C. P. brand of the salt was dissolved in freshly distilled water to form a saturated solution. Then 95 per cent alcohol saturated with paraffin was added to precipitate the hydrate, $FeSO_4 \cdot 7H_2O$.[2] The salt was collected and allowed to dry on porous porcelain and then kept in a bottle covered with black paper. In this way, on account of the adsorption of the paraffin on the surface of the salt, the ferrous salt was well protected from oxidation for a long time.

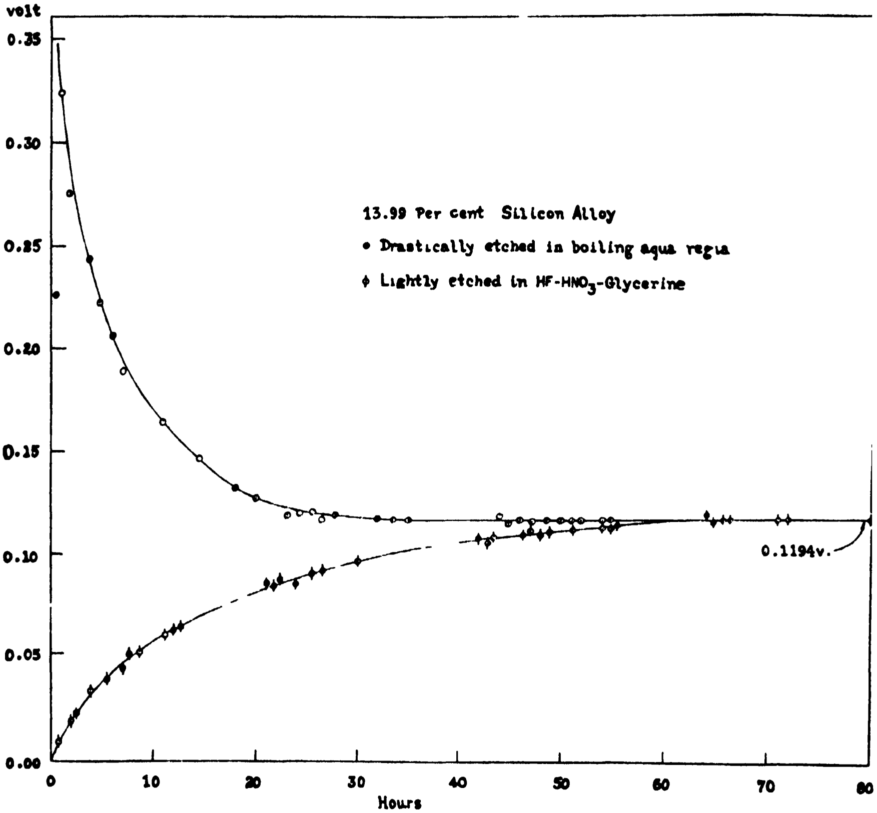

FIG. 4. THE CHANGE IN THE ELECTRODE POTENTIAL OF AN IRON–IRON-SILICON ALLOY WITH RESPECT TO TIME

Note that the equilibrium is approached from both sides

[2] The salt was merely assumed to be the heptahydrate; no actual analysis was made.

In figure 4 is shown a typical example of how an iron-silicon electrode comes to an equilibrium in the cell. The upper curve is that due to the alloy electrode that was etched in boiling aqua regia, while the lower curve is that due to the alloy that was etched less drastically with the HF–HNO_3–glycerine etchant. While the upper curve suggests polarization phenomena, the lower curve proves that this is not the case. The fact that equilibrium is approached from both sides indicates that the cell is apparently reversible. In the absence of other pertinent thermal data (e.g., entropy, heat of formation, etc.), we are unable at present to interpret the actual significance of

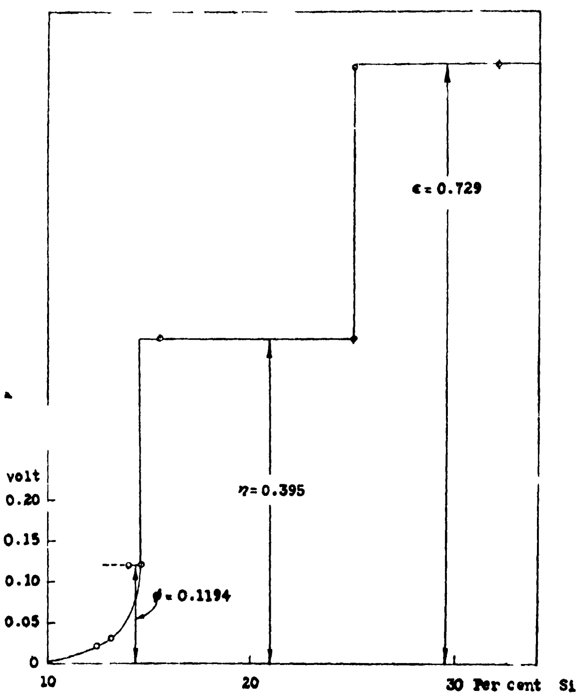

FIG. 5. THE ELECTRODE POTENTIAL OF SOME IRON-SILICON ALLOYS

the electrode potential, although the activity of iron can be directly calculated from equation 1. In the range up to 5 per cent silicon (by weight) the electrode potentials are very small, so that the influence of impurities and surface conditions becomes marked; no attempt was therefore made to measure **E** nor d**E**/dT.

Although theoretically the electrode potential of the 13.99 per cent silicon alloy should be much less than that of the compound ϕ, the observed potential is, however, that of the compound as shown in figure 5. This may be attributable to the fact that after long annealing at high temperatures, there must have been some tendency (present in all solid solutions) towards unmixing of the components in solution—in this case, apparently to iron and ϕ. If the solute were silicon, we would hardly have obtained the potential characteristic of ϕ. This suggests that the electrode potential method of determining the phase structure in an alloy is very sensitive. The existence of a compound Fe_3Si_2 (η) is also confirmed. That the compound is a result of a peritectoid reaction "$\phi + \epsilon \rightleftharpoons \eta$" is shown in a very interesting way as follows: a commercial 25 per cent silicon alloy showed a potential of about 0.725 volts in the "as cast" condition, indicating the presence of ϵ, but another sample in the annealed condition showed a potential of about 0.395 volts, which is the potential characteristic of η. It also appears from this observation that η does not form solid solutions with other impurities found in the commerical alloys and that the composition appears to be constant. The electrode potential of ϵ is about 0.725 to 0.729 volts, considerably higher than that of η.

MICROSCOPIC EXAMINATION OF THE ALLOYS

For the purpose of correlating the results, a microscopic examination of the alloys was made. It is quite true, as Corson pointed out, that no metallographic evidence has ever been produced proving conclusively the existence of the compound η. In the hope that the compound η might not belong to the isometric system, the writer used a polarizing microscope (Reichert make) in an attempt to detect its presence in the 15.56 per cent silicon alloy, but no positive confirmation could be obtained. In the case of the 13.99 per cent silicon alloy, the electrode potential indicates the presence of some ϕ and so the alloy was studied intensively to ascertain if ϕ can be distinguished from the ordinary solid solution. An attempt to study the inner symmetry of ϕ by means of etch figures failed, because even boiling aqua regia did not yield etch figures. The specimen was then placed in a ferrous sulfate solution and allowed to oxidize in the air for about one month. This resulted in the production of some etch figures (square and rectangular pits), but they were located in places where their position could not be correlated with respect to the large grains.[3] It should be noted here, however, that the microscopic evidence presented by Corson regarding the existence of ϕ is highly questionable in value. The "bushings" he observed were probably due to strains produced either in the process of cooling from the melt or during the polishing operation of the metallographic samples.

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[3] It was hoped that if segregation of ϕ had appreciably taken place within a large grain, the etch figures in one part of the grain might differ in orientation and shape from those in other parts of the grain where ϕ is localized. The only indirect evidence of ϕ in the sample lies in the fact that certain grains (rather small and located within a large grain) were apparently unattacked by any chemical reagent, however drastic the treatment.

X-RAY ANALYSIS OF THE ALLOYS

Although Phragmen had made a careful x-ray analysis of the iron–silicon alloys he prepared, he did not use as pure alloys as the present writer has under investigation. The alloys, although already annealed for 150 hours at 900°C., were given another 150 hour annealing at the same temperature and cooled down to room temperature in 24 hours in order to determine whether a hyperstructure might be formed in the alloys with less than 14.35 per cent silicon, as a result of further unmixing of the components in solid solution.

Although the accuracy of the x-ray measurements on films taken with the ordinary cassettes that come with the General Electric Co. apparatus is only of the order of ±0.005Å., the absolute error can be minimized as follows: If we use as a standard for comparison pure iron, whose lattice parameter is known accurately, then as the effect of silicon is merely to shift the diffraction lines, the absolute length of any diffraction line from zero beam can be calibrated each time against the known (calculated) length of the corresponding line for pure iron. In this way, irrespective of the shrinkage of the film (which is about 12 in. long) or slight inaccuracies of the cassettes used, the absolute error is thus reduced to about ±0.001Å. As a result of several sets of measurements, the lattice parameter of the electrolytic iron used by the writer was determined to be 2.860Å. The films were measured on a small "home-made" comparator accurate to about 0.002 cm.

The results of the present investigation are graphically shown in figure 6 in comparison with those obtained by Phragmen. According to him, an alloy of the composition 3Fe/Si is merely a distinguished point in a series of solid solutions. The fact, however, that the lattice parameter of ϕ obtained by the writer is the same as that found by Phragmen, while in the range of solid solutions appreciable differences occur, is cogent argument in support of the assumption that ϕ is a compound. According to figure 6, the limit of solid solution is exactly that represented by ϕ. The difference in our results may be explained as follows: As unmixing takes place, the solid solution decreases in concentration with respect to silicon, hence, the fundamental lattice constant of the solid solution should increase accordingly.[4] We should, therefore, expect the diffraction lines of both the solid solution and ϕ to be present, but this was not the case. It should be pointed out that the x-ray method is rather insensitive for the detection of small amounts of a second phase.

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[4] Since this work was completed, the writer has been able to increase greatly the accuracy of the G. E. cassette by a special device, on which a patent is being obtained. The pure alloys were unfortunately spoiled in the course of some other experiments. However, the 5 per cent silicon commercial alloy was again analyzed and was found to have a lattice constant of 2.856_2 Å based on pure sodium chloride.

With the composition represented by 3Fe/Si, it appears reasonable to assume with Phragmen that if we take twice the size of the unit cell of iron and distribute the silicon atoms at the corners and face-centered positions, we have what corresponds to the hyperstructure of ϕ, with a fundamental lattice constant of 5.630Å. On a film taken with a rotating Debye-Scherrer type of camera, the only additional line determined with some certainty was 311, although even mere faint traces were also found which could be ascribed to the 2 (100) and 2 (111) planes. Although this is thus a confirmation of the regular distribution suggested by Phragmen, the x-ray method cannot by itself determine whether ϕ is a solid solution or a compound, as it does not describe the force-field between the different atoms in the lattice.

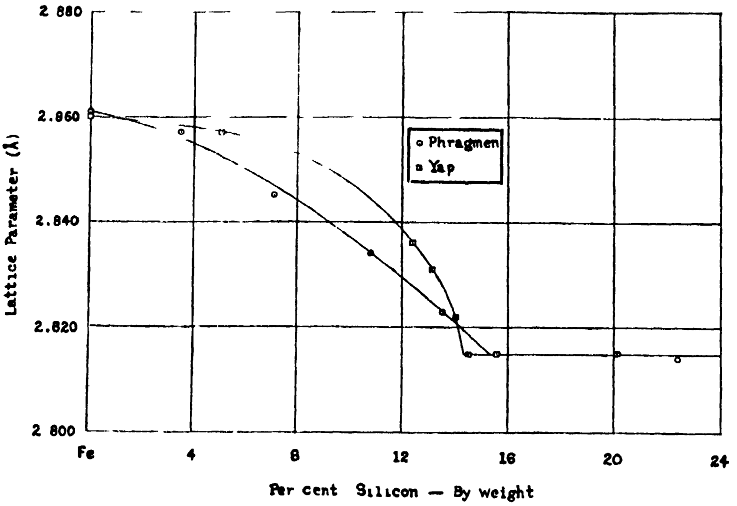

Fig. 6. The Change in the Size of the Unit Cell with Respect to Silicon Content

THERMODYNAMIC CONSIDERATIONS OF THE EQUILIBRIA

A critical study of the original papers by Tammann, Kurnakow, Gontermann, Sanfourche, *et al.*, reveals that their results can be consistently interpreted as showing a "singular point" in the liquidus–solidus curves at about 14.4 per cent silicon, although according to Haughton and Becker, the singular point is about 12.2 per cent silicon. If the singular point were at 14.35 per cent, then the phase diagram of the iron–silicon system could be easily represented as a composite of the following binary systems: Fe–Fe_3Si, Fe_3Si–FeSi, FeSi–$FeSi_2$ and $FeSi_2$–Si. In such a case, the phase rule itself justifies us, even in the absence of any kind of independent evidence, in treating Fe_3Si as a compound.

It can be shown from thermodynamics that in heterogeneous equilibria involving the melt and a solid that is a solid solution (2)

$$\frac{d \ln(a/a')_A}{d(1/T)} = \frac{\Delta H_A}{R} \tag{2}$$

in which a is the activity of A in the melt and a' its activity in the solid solution. When we substitute mole-fractions for activities, equation 2 reduces to

$$\frac{d \ln(N'/N)_A}{d(1/T)} = \frac{\Delta H_A}{R} \tag{3}$$

so that if we plot ln (N′/N) against $1/T$, the slope of the curve as $(N'/N) \doteq 1$ should give us the correct value of ΔH_A, the heat of fusion of the pure solvent at its melting point. We are here required to make some *a priori* assumption regarding the nature of the solute, when the solvent alone is a pure and simple substance, like iron. In figure 7, curve I is calculated on the assumption that the solute is in the form of silicon atoms. We know from thermodynamic considerations that a positive deviation from Raoult's law is normally associated with an absorption of heat and an expansion in volume, and a negative deviation is accompanied with the opposite effects; the former also indicates a tendency towards unmixing, while the latter indicates a tendency towards the formation of compounds (3). As ideal solutions are defined from the standpoint of Raoult's law, any deviation from Raoult's law will be indicated by the deviation from the ideal solubility curve.[5]

We note that curve I shows a large negative deviation, which thus indicates that the solute forms a compound with the solvent atoms. Hence, curve II is calculated on the assumption that the solute is Fe_3Si, which is also evidently incorrect, as it gives 108.5 calories per gram as the heat of fusion of pure iron. We note, however, that curve II is linear for some range of temperature and concentration, and this constant deviation indicates a definite change in the ratio of molar concentrations, or, what is equivalent to it, a change in the total moles taking part in the equilibria. If we thus assume the solute to be $(Fe_3Si)_2$,[6] then we obtain curve III, which gives the correct heat of fusion of iron, 65 calories per gram as the curve approaches the concentration pure iron, that is, as (N′/N) $\doteq$ 1.

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[5] In a strict sense, when solid solutions are involved in the equilibrium with the melt, the term "ideal solubility curve" is meaningless, as each solute will have a characteristic distribution constant.

[6] It is indeed curious—perhaps entirely accidental—that all compounds in the iron-silicon system can be represented by Fe_6Si_n, where n is an even number. It may be recalled that silicon, like GeGe, GeAs, ZnSe, ZnS and CC (diamond) is of the covalent type and may be considered diatomic. In view of this fact, the assignment of the formula $(Fe_3Si)_2$ or Fe_6Si_2 becomes reasonable.

Just what is the real significance of polymerized molecules of $(Fe_3Si)_2$ existing in the melt and in solid solution, the writer is unable to say at present; neither is he interested in building up a mechanistic picture of such a compound. In the final analysis, provided the determination of the liquidus and solidus curve is sufficiently accurate and the heat of fusion of the solvent metal is known, the constitution of the solute in solution is revealed with some certainty by the thermodynamic laws relating to the depression of the freezing point. There are, of course, other sources of evidence of the reality of the existence of molecular solutes in the liquid state (e.g., studies in magnetic susceptibility, resistance, specific volume, Raman spectra, etc.), although the existence of the molecular solute in solid solution is much more difficult to prove. Given a saturated metallic solid solution in equilibrium with some excess solid solute in the form of an intermetallic compound AB; the common conception is that AB is dissociated to A + B upon dissolution in the solid solution. It is difficult to conceive, from strictly thermodynamic considerations, of the solute molecules magically dissociated in solution and yet in equilibrium with the solid solute (AB) whose dissociation pressure may be extremely small. I have already pointed out elsewhere (4) that if this were true, it should then be easy enough to construct a perpetual machine by simply lowering and elevating the temperature of a saturated solid solution.

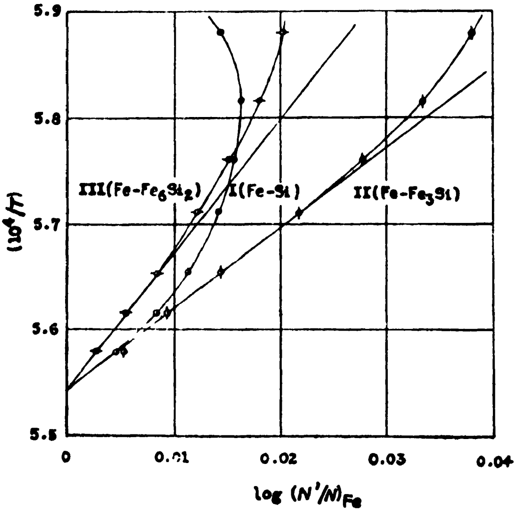

FIG. 7. THE LOG (N′/N).T^{-1} CURVES PLOTTED ACCORDING TO EQUATION 3

In order to ascertain if the degree of error in the thermal analysis can adequately account for the displacement of curve II in figure 7 from the ideal position, backward calculations were made on the assumption that the solidus is correct, as it was determined by Haughton and Becker by the Heycock-Neville method.[7] The calculated error in the location of the liquidus appears too large to be accounted for in this manner. The effect of silicon vapor on the reproducibility of a thermocouple is well-known and the accuracy of the thermal analysis of the primary solidification range may not be any better than ±5°C. On this assumption, the liquidus and solidus curves drawn by Haughton and Becker have been redrawn as shown in figure 8, in which $(Fe_3Si)_2$ is shown to have a definite melting point at 1250°C.

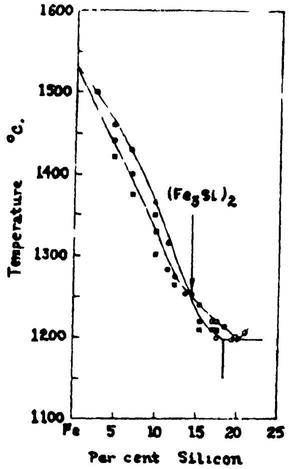

FIG. 8. THE PRIMARY SOLIDIFICATION RANGE OF IRON–SILICON ALLOYS (AFTER HAUGHTON AND BECKER)

STABILITY OF SOLID SOLUTIONS

Some remarks regarding liquation (i.e., unmixing) and consequent segregation of the components in solid solution may not be amiss in this paper. Let us conceive of a metallic system, A and B, which forms a complete series of solid solutions and in which no compounds are formed in the melt. The free energy of the system is at a minimum when A and B are distributed in such a manner that any unit portion (say a unit cell) has the same free energy content as any other unit portion. It is obvious that in a cubic system this condition is attained in the solid state only when the atomic fraction is a multiple of 1/8 when the solute atoms can be assigned a definite position in the space lattice. This is the basis of Tammann's conception of regular distribution as "limits of resistance," as opposed to Vegard's view of the atoms being statistically (irregularly) distributed. In the liquid state where the atomic (and molecular) mobilities are much higher than in the solid state, a statistical distribution satisfies our conception of a homogeneous system, characterized by the lowest free energy; on the other hand, a solid solution may be expected to approach true homogeneity only as it approaches some form of regular distribution. When a solid solution is truly homogeneous, its free energy per mole (or gram-atom) is given by the equation

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[7] The Heycock-Neville method involves quenching alloy specimens to successively higher temperatures and then examining the structure microscopically. The structure will be quite characteristic when the solidus temperature is reached.

$$F = \text{N}_1\bar{F}_1 + \text{N}_2\bar{F}_2 = RT(\text{N}_1 \ln a_1 + \text{N}_2 \ln a_2) \qquad (4)$$

where $\bar{F}_1$ and $\bar{F}_2$ are the partial molal free energies of transfer of A and B (indicated for convenience by subscripts 1 and 2, respectively) from the pure state to a solid solution of activities a_1 and a_2, respectively. When the system obeys the laws of ideal solution, then $a_1 = \text{N}_1$ and $a_2 = \text{N}_2$ and their respective activities will vary linearly from 1 to 0 as shown in figure 9. The activity–composition curves (1′) and (2′) indicate a negative deviation, hence a tendency towards compound formation.

If the activity–composition curves were something like those shown in figure 10, all solid solutions between the composition of X and Y will have a tendency towards unmixing, whilst between A and X and between Y and B, a strong tendency towards compound formation exists (5). The problem then arises as to which of these two opposing tendencies is the more dominant and under what conditions one is more likely to occur than the other. From strictly graphical analysis of the phase diagram, when the solidification range of the solid solutions is wide, we may reasonably anticipate the system to show a tendency to liquate.[8] When the liquidus and solidus curves are very close together, then the solid solutions will melt over such a small temperature range as to behave as a unary substance, i.e., as a compound in this case. It should be noted, however, from phase-rule considerations, that as long as we have a solid solution, there will be a temperature range of melting, however small.

The problem now arises as to whether or not a regular distribution is a compound. According to our strict interpretation of homogeneity (based on the elementary cell as a unit) a regular distribution merely represents an extreme form of an ideally homogeneous distribution in the solid state, but it is also self-evident that we are stretching the criterion of homogeneity much further than is warranted even in the case of liquid solutions. It is thus quite conceivable that even if the unit of homogeneity were a thousandfold larger than an elementary cell, an aqueous solution might likewise appear to be inhomogeneous, especially if the solute molecules were quite large. Let us, therefore, seek elsewhere some other criterion of the nature of a regular distribution. In the first place, it cannot be denied that some sort of chemical affinity is implicit in the tendency towards a regular distribution, because there is absolutely no reason on the basis of probability why the solute atoms can be made to distribute so regularly in the space lattice. If a regular lattice merely represents a special form of solid solution, whose free energy is at a minimum, then the perplexing question arises as to why once the regular distribution is obtained, it can be destroyed again by merely heating up to a certain temperature and cooling down rapidly.

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[8] This fact will become more evident when we recall that the phase diagram of two substances completely immiscible in each other in the solid and liquid states is given by two horizontal lines erected at their respective melting points, extending from one component to the other; if the liquidus and solidus curves become spaced wider and wider apart, naturally they will approach, as a limit, these two horizontal lines.

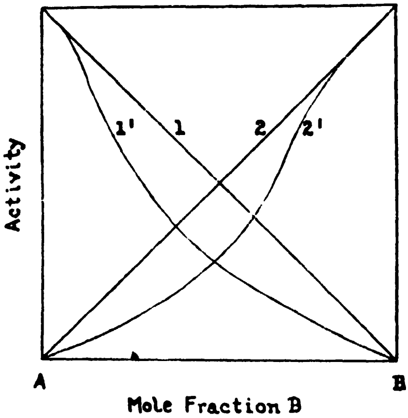

Fig. 9

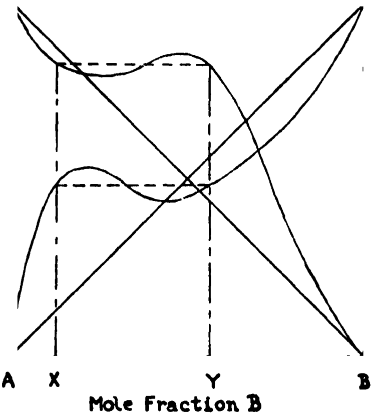

Fig. 10

Fig. 9. Activity–composition Curves

The linear activity–composition curves 1 and 2 indicate that the solid solutions are ideal from A to B. The negative deviations of the activity–composition curves 1′ and 2′ indicate a strong tendency to compound formation, although the compound formation is incomplete.

Fig. 10. Activity–composition Curves

The activity–composition curves indicate a tendency to compound formation between A-X and Y-B and a tendency to liquation between X-Y.

On the assumption that a regular distribution is a compound, the critical temperature then corresponds to a melting phenomenon in the solid state. When the solvent and solute atoms have some affinity for each other to form compounds, their size and shape must undergo some alteration as a result of the alteration in their electronic configurations (e.g., as due to sharing of electrons) and consequently their crystallographic habits will likewise be modified. The larger the affinity, the more marked will the alteration be, so that the compound may actually crystallize in an entirely different system, although it should be noted that often it is simply a matter of changing the crystallographic axes of reference.[9]

It is certainly curious that a solid solution, in its tendency to liquate or unmix and to form a regular structure, behaves like a dispersed system. A system in which all the dispersed particles are of the same size and therefore, possessing the same surface energy per particle, may theoretically be expected to be rather stable and should show little or no tendency towards aggregation; it is only owing to the difference in the surface energy of the dispersed particles of varying size that we have a tendency towards aggregation,[10] which may eventually lead to two equally stable states, viz., (1) a state in which the dispersed particles finally aggregate into a single large particle and (2) a state in which all particles again assume the same, though larger, particle-size. The former state is equivalent to the liquation tendency in solid solutions described above, while the latter is similar to the tendency to form a regular distribution. The writer hopes to work out these theoretical relationships in more detail in the future.

SUMMARY

1. On the basis of the results obtained in the study of some iron-silicon alloys of high purity, by means of the thermoelectric method, electrode potential measurements and x-ray crystal analysis, it is concluded that Fe_3Si (ϕ) is a compound and not merely a distinguished point in a series of solid solutions. The existence of Fe_3Si_2 (η) and FeSi (ϵ) is also indicated by the electrode potential measurements, without direct evidence, however, of their actual chemical composition.

2. By the thermodynamic method of studying the depression in the freezing point, it is shown that the actual composition of ϕ is $(Fe_3Si)_2$ or Fe_6Si_2.

3. In the hope of helping to clarify some of our conceptions regarding the stability of solid solutions, the tendency to liquation (i.e., unmixing) and formation of regular distribution, has been discussed at some length from

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[9] To illustrate: If A and B crystallize in the face-centered cubic system, but the regular distribution crystallizes in the body-centered tetragonal system with, say, $c/a = 1.5$. Then if we choose different crystallographic axes of reference for the face-centered cube and treat A and B as crystallizing in the body-centered tetragonal system with $c/a = 1.414$, the crystallographic differences become much less and more understandable.

[10] This is because the system is not in equilibrium, because although the usual parameters of the free energy (pressure, temperature, and composition) are defined, the change in the free energy with respect to the surface $(\partial F/\partial\sigma)_{P,T,N}$ has not been determined. Hence, the system will possess an additional degree of freedom.

the thermodynamic point of view. Reasons why a solid solution with a regular distribution should be treated as a compound, have been advanced.

The facilities for carrying out this investigation in the Department of Chemistry, Washington Square College of New York University, were kindly provided by Professor Ehret (who read the proof in the absence of the author), and to him and to Professor King the writer desires to express his cordial thanks for their friendly interest and suggestions during the progress of the work. Special mention should be made of the diligent assistance of Messrs Diller and Abramson—the former for making the thermoelectric study, and the latter for taking numerous electrode potential readings.

REFERENCES

(1) HAUGHTON, J L , AND BECKER, M J Iron Steel Inst London **121,** 315 (1930).
STOUGHTON, B , AND GREINER, E S : Trans Am Inst Mining Met. Engrs , Iron and Steel Division, p 155 (1930)
CORSON, M G . Trans Am Inst Mining Met Engrs , Iron and Steel Division, p 249 (1928)
MURAKAMI, T Science Repts Tôhoku Imp Univ **10,** 79 (1921); **16,** 475 (1927)
PHRAGMEN, G · J Iron Steel Inst London **114,** 397 (1926)
BAMBERGER, M , EINERL, O , AND NUSSBAUM, J Stahl u Eisen **44,** 141 (1925)
KURNAKOFF, N , AND URAZOFF, G Z anorg chem **123,** 89 (1922)
SANFOURCHE, M A Rev mét **16,** 217 (1919)
GONTERMANN, W : Z anorg Chem **58,** 384 (1908)
GUERTLER, W , AND TAMMANN, G Z anorg Chem **47,** 163 (1908)
(2) YAP, C P : Trans Faraday Soc **27,** 777 (1931)
(3) HILDEBRAND, J H Solubility Chemical Catalog Co , New York (1924)
(4) Consult for example, a recent paper on the system NaCl–AgCl by A WACHTER: J Am Chem Soc **54,** 919 (1932)

THE MOLECULAR WEIGHTS OF SOME DISSOLVED SUBSTANCES

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The molecular weight of a polymer of phenylacetaldehyde when it was dissolved in seven solvents, was determined by one of us, using the freezing point method (1). The molecular weight was about 360 in six solvents, indicating the molecule $(C_8H_8O)_3$, but the molecular weight was believed to be about 720 in bromoform and to indicate $(C_8H_8O)_6$. It was thought that other examples of similar behavior might be found, especially among substances which exist in different modifications in the solid state or as amorphous solids. Such has not been confirmed, except for the association of some organic acids in benzene, bromoform, and paraldehyde towards the bimolecular form,—a fact which has long been known. Moreover the high molecular weight obtained for the phenylacetaldehyde polymer in bromoform was proved to be wrong; this result was due to the bromoform being moist (or impure).

The molecular weights of the various solutes were found by Raoult's method, using Beckmann thermometers and working in a current of dry air when necesary. The approximations of the method have at least been more fully realized. Thus with aniline, for example, the supercooling was so serious that only the molecular weight of the phenylacetaldehyde polymer was determined in this solvent. And with anethole the supercooling was so serious and the subsequent rate of crystallization so slow that correct freezing points could not be obtained. Again, the lag in a Beckmann thermometer is sometimes large, or there is a slow rise of the readings after a previous exposure to a higher temperature; also the exposed-stem correction may become appreciable, and variable if the sunlight falls directly on the thermometer. While the difference in the freezing points of solvent and solution should not, with the usual apparatus, be less than 0.1°C. if results are to be obtained with an accuracy of about 2 per cent, however, even with ordinary precautions the results may vary disconcertingly; also the theoretical imperfections from Raoult's law, or from the behavior of ideal dilute solutions, may render the results approximate. The variations in Raoult's constant, as quoted from different observers for a given liquid, themselves indicate the approximations which may be expected in the molecular weights thus found (2).

In our work the following were taken as Raoult's constants, or the molecular depressions of the freezing point for 1 g. of solute in 100 g. of solvent:—benzene, 51; bromoform, 144; phenol, 72.7; acetic acid, 39, paraldehyde, 70.5; aniline, 58.7.

A new sample of phenylacetaldehyde polymer was prepared by washing away the unchanged phenylacetaldehyde with alcohol, and then by drying the residue over sulfuric acid for a month. The polymer was subsequently kept over calcium chloride. The polymer consisted of definite needle-shaped crystals (rhombic ?). Its melting point was 104.5°C. Samples of this polymer were dissolved and recrystallized, or recovered, from carbon tetrachloride, benzene, and ether, as similarly shaped crystals. The melting points of these samples were 103.5°C., 105°C., and 103.5°C., respectively, the lower values being probably the better. These samples had the same molecular weights in bromoform, benzene, and phenol within the limits of the experimental errors.

A number of experiments with bromoform indicated that the molecular weights here seemed to come high readily, or the freezing points of the solutions tended to be high, which was disconcerting as in these experiments the maximum temperatures are usually taken as the true freezing points. Thus various samples of the phenylacetaldehyde polymer gave in bromoform the molecular weights 375, 389, 393, 294, and 360. Other experiments clearly showed that with moist bromoform high results were obtained for the molecular weights, and the first three of the above results are so affected; in the fourth result the depression of the freezing point was small, but the last experiment was done with every precaution to keep the bromoform dry. The bromoform is best purified by distillation, followed by drying over potassium carbonate, and by freezing out; it remains colorless over potassium carbonate. In the above experiments the depressions varied from 0.100°C. to 0.540°C., and the concentrations from 0.26 to 1.46 g. of solute per 100 g. of solvent.

In aniline the phenylacetaldehyde polymer had the molecular weight of 335, this value being corrected for the supercooling (1.6°C.) of the solution, the concentration of which was 0.706. This solvent not only gave excessive supercooling but was also extremely hygroscopic.

In phenol and in acetic acid the phenylacetaldehyde polymer also existed in the trimolecular form, which therefore was its constant form in all the solvents examined.

Paraldehyde was found to be trimolecular in benzene, phenol, bromoform, and acetic acid; it is also trimolecular in water (3).

Metaldehyde was prepared from acetaldehyde; its melting point in a sealed tube was 140°C. Unfortunately it was not soluble in the solvents at

TABLE 1

Molecular weights found

The concentrations of the solutions (grams of solute per 100 g. of solvent) are given in parentheses.

SOLUTE	EMPIRICAL M	SOLVENT				
		Benzene	Bromoform	Phenol	Acetic acid	Paraldehyde
Phenylacetaldehyde polymer	120	356 M_3 (1.3-2.0)	360 M_3 (0.2-1.5)	368 M_3 (0.86)	363 M_3 (0.60)	403 M_3 (0.38)
Paraldehyde	44	132 M_3 (3.66)	128 M_3 (0.24-0.6)	123 M_3 (0.78)	138 M_3 (1.58)	—
Anisaldehyde	136	142 M (2.1)	149 M (0.57)	145 M (0.82)	148 M (1.90)	—
Cinnamaldehyde	132	136 M (1.3-2.4)	148 M (0.43)	133 M (0.48)	114 M (0.89)	—
Benzophenone	188	168 M (6.93)	173 M (0.39)	187 M (0.78)	192 M (0.93)	181 M (1.04)
Phthalic anhydride	148	—		160 M (0.66)	156 M (0.85)	160 M (0.43)
Cinnamic acid	148	264 M_2 ⇅ (0.53) M	302 M_2 (0.27)	161 M (1.03)	149 M (1.3-0.6)	243 M_2 ⇅ (0.43) M
Phenylacetic acid	136	217 M_2 ⇅ (1.04) M	269 M_2 (0.59)	153 M (1.40)	150 M (1.50)	214 M_2 ⇅ (1.04) M
Benzoic acid	122	244* M_2 (1.4)	254 M_2 (0.49)	137 M (1.26)	136 M (1.57)	194 M_2 ⇅ (0.97) M
Rhombic sulfur	32	242 M_8 (1.04)	253 M_8 (0.18)	—	—	—
Monoclinic sulfur	32	260 M_8 (0.45)	246 M_8 (0.45)	—	—	—

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* Roloff: (1895). See Seidell's Solubilities of Inorganic and Organic Substances.

our disposal, except in phenol. In phenol three experiments, at concentrations 0.659, 0.655, and 0.578, gave the molecular weights 165, 146, and 147—mean = 153; this is just about the mean between the trimolecular and the tetramolecular forms.

Paraformaldehyde was dried over sulfuric acid for days: it was apparently crystalline under the microscope. It melted in a closed tube at 155–160°C., resolidifying on cooling; it sublimed from about 135°C. in the closed tube. It was insoluble in the usual solvents, but it dissolved in phenol slowly, giving a strong smell of formaldehyde. The molecular weight in phenol (concentration = 0.65) was 35, indicating complete dissociation ($CH_2O = 30$).

Anisaldehyde and cinnamaldehyde were unimolecular in all the solvents examined, as also were phthalic anhydride and benzophenone. The ordinary stable form of the latter substance was used.

Rhombic and monoclinic sulfur were examined in benzene and in bromoform; in both of these solvents, however, the sulfur is not readily soluble. The depressions of the freezing point were small, but they indicated octatomic molecules, S_8, in both solvents for both solutes.

Benzoic, cinnamic, and phenylacetic acids behaved similarly. In benzene, bromoform, and paraldehyde these acids were partly associated, nearly completely to the bimolecular stage in the first two solvents, and about half-way to that stage in the paraldehyde. But it is well-known that their degrees of association depend on the concentrations in solution. In phenol and in acetic acid, however, these three acids were (within the limits of error) unimolecular.

Table 1 gives the chief results. Here the molecular weights obtained are quoted, with the concentrations (g. of solute per 100 g. of solvent) set underneath in brackets and showing where duplicate experiments or more were done; also the molecules existing in the solutions are indicated.

The authors wish to thank the Council for Scientific and Industrial Research, Australia, for a grant towards the expenses of the investigation.

REFERENCES

(1) Pound, J. R.: J. Phys. Chem. **35**, 1174 (1931).
(2) Lewis, P. B.: J. Chem. Soc. **67**, 1 (1895). A description of Raoult's method applied with extreme precautions.
(3) Pascal and Dupuy: Bull. soc. chim. **27**, 353 (1920).

NEW BOOKS

Matiere et Energie. By VICTOR HENRI. 436 pp. Paris: Hermann et Cie, 1933. Price: 110 francs, unbound.

The influence of the new molecular physics is constantly felt with increasing and expanding force both by the layman and also within the realms of science itself. It is not a cause for wonder that men of science feel attracted to the subject with such force as often to be impelled to record the results of the new acquisitions in book form, even when in a field in which they may not previously have been actively engaged.

That Victor Henri, so well-known for his contributions to spectroscopy and photochemistry, has succeeded in presenting a laudable monograph in molecular physics, there will be no doubt on the part of the reader. He has approached the subject from a charmingly individual and philosophical point of view and maintains throughout a closeness of contact with the other more classical fields of chemistry and physics which convince the reader of the breadth of his grasp of the subject in its entirety.

The subjects treated are: the discontinuity of matter—determination of the number of molecules; the chemical elements and the properties common to all elements—Roentgen spectra, atomic number; the periodic system; radioactive elements, isotopes; disintegration and synthesis of elements—their spatial properties in solids and liquids; the kinetic gas theory; the structure of atoms, including a splendid history of the subject from pre-Bohr theories to those of the present time.

In the chapter on isotopes an extended table giving the hypothetical constitution of nuclei according to Heisenberg is given and the supposed ratio of neutrons:protons in each species of element.

In a work apparently quite free from errors one is surprised to find—in at least two citations—the discovery of the refraction of electrons credited to Davison and Kunsman instead of to Davison and Germer.

S. C. LIND.

Die Alkalichlorideleklrolyse in Diaphragmzellen. Eine Theoretische und Experimentelle Untersuchung. Part I. By GOSTA ANGEL. 126 pp. Berlin: Verlag Chemie, G. M. B. H., 1933. Price: 12 M.

This book, which is divided into four parts, represents a four year investigation on alkali chloride electrolysis in diaphragm cells. The work was carried on in the electrochemical laboratory of the Kgl. Technische Hochschule at Stockholm.

Part I (37 pp.). A general review of the subject, including the work of other investigators. A detailed presentation of the theory is made and a number of equations are given for estimating the quantitative relations existing between the rate of flow of sodium chloride, the current flowing, the current yield in sodium hydroxide in per cent, the moles of chloride per liter in the anolyte and catholyte, and the transference number of the cation. This material is clearly presented with the aid of ten curves and seven tables of data.

Part II (32 pp.) Experimental results. A detailed picture of the experimental cell and analytical methods used is given, together with nine tables of data and three curves. The experimental results served to test the theoretical equations given in Part I. Much careful work was done and good agreement with the theory was found.

Part III (24 pp.). Eleven tables and nine curves are used to present the properties of the sodium chloride and sodium hydroxide solutions giving the specific gravity, the relative viscosity, and specific conductivity of various concentrations of salt solutions at temperatures from 18°C. to 70°C. The influence of these variables on cell operation is discussed in considerable detail.

Part IV (20 pp.). In this section the author gives equations and data for the electrolysis of potassium chloride solutions. Three curves and seven tables of data are given. The general nature of the equations for potassium chloride is similar to those for sodium chloride, but the quantitative results are somewhat different These differences are carefully defined and clearly explained.

This book combines a nice presentation of theory with careful experimental work. The many curves and tables summarize and coördinate the material into a readily usable form which will be of interest not only to scientific workers but also to those engaged in the commercial applications of alkali chloride electrolysis.

G. H. Montillon.

The Scientific Achievements of Sir Humphry Davy. By Joshua C. Gregory, B. Sc., F. I. C. 12.5 x 19 cm.; vii + 144 pp. New York: Oxford University Press, 1930. Price: $2.00.

This compact little volume is an exposition of Davy's experimental and theoretical contributions. Although it does not, like certain other biographies, trace in detail the entire course of Davy's life, it does introduce in chronological sequence enough well-chosen biographical material to explain the origin of the great conceptions which developed in Davy's mind.

In his first paper, written at the age of nineteen years, Davy had the temerity to oppose certain aspects of Lavoisier's theory of combustion. To explain the light which accompanies rapid combustions, the youthful chemist postulated the existence of *phosoxygen,* a compound of oxygen and light; the accompanying heat he regarded as a "repulsive motion" of particles. The outstanding investigation at Dr. Beddoes' Pneumatic Institution was the famous study of the physiological properties of nitrous oxide. Readers who have a sense of humor will heartily enjoy the author's paragraphs on the behavior of Davy's "patients."

Before discussing Davy's astonishing electrochemical successes, the author describes the state of consternation which resulted from Nicholson and Carlisle's decomposition of water with the voltaic pile. To a contemporary, the evolution of hydrogen and oxygen from *separated* wires seemed utterly incomprehensible. When the two poles of the battery were placed in separate vessels connected by a siphon, "the oxygen and hydrogen still fizzed off separately . . . When oxygen streamed off at one wire, the hydrogen with which it had been combined had apparently to scamper through the siphon to stream off at the other wire." Davy's experiments led him to a rational explanation of this phenomenon and the isolation of the alkali and alkaline earth metals. Since many properties of the metals could be explained by assuming that they contain hydrogen, Davy pondered over, but did not adopt, a revised phlogiston theory in which this hypothetical principle of flammability was identified with hydrogen.

After reading of the difficulties which Davy had to overcome in order to prove the elementary nature of "oxymuriatic acid," one readily understands what a revolution in chemical thought is implied in the words "chlorine" and "hydrochloric acid." The paragraphs on the safety-lamp for miners show the lofty side of Davy's character as he "refused to put 'four horses' to his 'carriage' by patenting his invention." The chapter on Davy and Dalton is an interesting character study. Although Davy avoided the word "atom" because it implies indivisibility, he honored Dalton for "fixing the *proportions* in which bodies combine."

Since the volume makes possible a truer and fuller appreciation of the mental acumen of Sir Humphry Davy, it should prove to be of permanent value to chemists.

MARY ELVIRA WEEKS.

La Structure de la Cellulose dans ses Rapports avec la Constitution des Sucres. By G. CHAMPETIER. 16.5 x 25 cm.; 28 pp. Paris: Hermann et Cie, 1933. Price: 8 francs.

This little booklet is an excellent concise review of the present state of our knowledge regarding the structure of cellulose and its parent sugar, glucose. A brief historical review of the development of the structure of glucose ending with the work of Haworth and his school on the structures of stable and labile glucose is followed by a discussion of the new structural formulas of glucose and cellobiose proposed by Haworth. The second part of the monograph dealing with the structure of cellulose discusses celluloses from different sources, the hydrolysis of cellulose, and the light shed on the problem by x-ray crystal studies of Sponsler and Dore, and Meyer and Mark. The form and length of the hexose chains and their arrangement in cellulosic fibres is discussed, followed by a brief review of the principal reactions of cellulose and their relation to the proposed structure. The final section is devoted to the dimorphism of cellulose, in which field the author has made contributions. Although presenting nothing essentially new, this little monograph is valuable reading for anyone wishing a collected modern view of the evidence relating to the structure of this important polysaccharide.

RALPH E. MONTONNA.

Thermodynamics. By ALFRED W. PORTER, D. Sc., F. R. S. viii + 96 pp.; 22 figures. New York; E. P. Dutton and Co., Inc., 1931.

This small volume is one of a series of monographs on physical subjects and is written by an expert for students of physics rather than for students of chemistry. The introductory chapters dealing with the historical development of the subject are possibly the most useful portions of the book. They could be read with profit even by those who consider themselves well acquainted with thermodynamics.

F. H. MACDOUGALL.

An Outline of Wave Mechanics. By N. F. MOTT. 155 pp. Cambridge, England: The University Press, 1930.

The author attempts in eight short chapters to deal with the new wave mechanics, and it is remarkable that he can condense such a wealth of information into such a small space! He succeeds remarkably well, although he abbreviates the mathematical treatment at times just at the place where the non-mathematical reader would want more details. However in such places ample references are given so that the interested student can follow up the subject if he has the perseverance and the necessary mathematical skill. Moreover the author states in his introduction that he has written the book for advanced students in physics and for research workers. The eight chapters cover the following subjects: I. Waves and Particles II The Wave Equation. III. Group Velocity and the Uncertainty Principle. IV. The Theory of Stationary States. V. The Absorption of Radiation. VI. The Helium Atom and the Hydrogen Molecule. VII. Dynamics of Systems Containing Many Electrons. VIII. The Spin of the Electron and the Exclusion Principle. The book is quite convenient as a reference volume. A few printer's errors will give no trouble to the interested reader.

GEORGE GLOCKLER.

Grundbegriffe der Chemie. By E. Rabinowitsch. 151 pp.; 2 figs. Sammlung Goeschen. Berlin and Leipzig: Walter de Gruyter and Co., 1930.

The fundamentals of chemical thought are told in as concise a manner as is possible in such short space. This forced brevity makes the book of little value to the uninitiated, but the reader conversant with physical and chemical thought will find the little volume an interesting review of chemical theory. It should be of especial interest to American students of chemistry who wish to improve their knowledge of chemical German, for the style is very clear and the book maintains the high standard of this collection of scientific writings.

George Glockler.

The Quantum Theory. By Fritz Reiche. Translated from the German by H. S. Hatfield and H. L. Brose. London: Methuen & Co., Ltd., 1931.

This little volume contains an excellent treatment of the earlier quantum theory, —Planck to Bohr. It is very readable and should serve well students who wish to become acquainted with the earlier developments. The additional notes and references are very helpful and anyone desirous of studying in the field of modern theoretical atomic and molecular physics could well start his course with this volume. No attempt is made to take the newer theories of wave mechanics into account, although they are introduced in the later chapters and a sufficient number of references are given to enable one to go to the original literature. Moreover, individuals already acquainted with the topics dealt with will enjoy the treatment accorded the subject, and it is well worth anyone's time to read this book.

George Glockler.

Die Chemische Emissions Spektralanalyse. By W. Gerlach and E. Schweitzer. 120 pp; 35 figures. Leipzig: Verlag von L. Voss, 1930.

The authors cover mostly their own work and experience in the spectroscopic analysis of metals. The fundamental principles and the equipment used in both qualitative and quantitative procedure are discussed in seven chapters. The reader can get a fair idea of both the successes and the difficulties of this mode of analysis.

George Glockler.

Vorlesungen uber Wellenmechanik. By A. Lande. 132 pp.; 15 figures. Leipzig: Akademische Verlags Gesellschaft m. b. H., 1930.

These lectures were given by Professor Lande at the Ohio State University, Columbus, Ohio, and cover the field as it had been developed at the time. Since so many topics are treated it follows that the statements of individual problems are very brief, and the book should be most satisfactory to the student who already has a good knowledge of this branch of modern physics. Anyone building a library on quantum mechanics will be glad to add this summary of the subject to his collection, and to use it as a reference book.

George Glockler.

Les Théorèmes de Conversation dans la Théorie des Chocs Électroniques. By L. Goldstein. 26 pp. Monograph No. 70 of the scientific and industrial series published by Hermann & Co., Paris, 1933.

This volume is the ninth of the series on theoretical physics published under the direction of Professor L. de Broglie. The author shows by the mathematical methods of wave mechanics, using Born-Dirac collision theory, that the laws of conservation of energy and momentum are contained within the frame-work of these theories.

George Glockler.

A STUDY OF THE EFFECT OF SALTS ON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM

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Although there have been numerous studies (1) of the catalytic decomposition of hydrogen peroxide by various colloidal systems, the effect of neutral salts has been investigated in detail in only a few cases. Lottermoser and Lehmann (2) studied the effect of a number of neutral salts and hydroxides on the catalysis of the reaction by colloidal manganese dioxide. In this laboratory, Kepfer and Walton (3) investigated the effect of electrolytes on the catalytic decomposition by colloidal ferric oxide. Except for the work of Kastle and Loevenhart (1) no extensive study seems to have been made of the effect of electrolytes on the catalytic decomposition of hydrogen peroxide by an electrocolloid of the type of Bredig's platinum sol.

In the case of colloidal ferric oxide, Kepfer and Walton obtained results which indicate that there is a general retarding effect of neutral salts which is connected with their adsorption on the surface of the colloidal particles. It does not seem to be conclusively established, however, that this is a general effect of neutral salts on all colloidal catalysts. With colloidal manganese dioxide, Lottermoser and Lehmann state that the addition of alkali salts in considerable concentration exerts only a feeble retardation on the decomposition of hydrogen peroxide. Bredig and his coworkers (4), in studying the catalysis by several electrocolloids, found some salts to be effective and others ineffective.

The present investigation was undertaken to study in some detail the effect of various salts on the catalytic decomposition of hydrogen peroxide by colloidal platinum, and to determine, if possible, whether a general adsorption effect is obtained (as with colloidal ferric oxide) or a specific effect which might be attributed to the chemical constitution of the colloid surface.

It appeared that some knowledge of the changes in the surface of the colloid could be gained by measuring the change in migration velocity of the particles in an electric field. In this way it might be shown what relation exists between adsorption of ions by the colloid and the change in the catalytic activity.

EXPERIMENTAL

Reagents

The colloidal platinum solution was prepared by Bredig's method. The sol was allowed to stand for several days and then siphoned off to remove the precipitated particles. A portion of the stock solution was diluted to a concentration convenient for use in the experiments and was preserved in a thoroughly steamed-out Pyrex flask. This diluted portion was used in all the experiments.

The hydrogen peroxide was Merck's "reagent" quality superoxol, redistilled in an all-quartz system under reduced pressure, diluted with conductivity water to approximately 0.25 *M*, and kept in quartz flasks. All the water used was prepared in a conductivity water still, then redistilled in a quartz apparatus, and kept in steamed-out Pyrex flasks.

Method of procedure

The reaction was carried out at 25°C. in Erlenmeyer flasks, which were repeatedly cleaned and steamed before using. A definite order of adding the reagents was adhered to, since, as will be shown later, it has an effect on the rate of decomposition in certain cases. Thirty-five cc. of hydrogen peroxide solution was first placed in the flask, followed by 2 cc. of electrolyte solution of the concentration desired. After a few minutes 1 cc. of the platinum sol was added, and the solution thoroughly mixed by shaking. After 1 minute 4 cc. was titrated in acid solution by standard potassium permanganate. This was taken as the titration at zero time, and similar titrations were made at 15 minute intervals. Two or more duplicate runs were made on each solution. Velocity constants for a unimolecular reaction were calculated, and the time required for 50 per cent decomposition of the hydrogen peroxide was obtained.

MEASUREMENT OF THE VELOCITY OF MIGRATION OF THE COLLOIDAL PARTICLES IN AN ELECTRIC FIELD

The stability of a lyophobic sol is almost entirely due to a potential difference between an adsorbed surface layer and a relatively diffuse surrounding layer of oppositely charged ions. The migration velocity of the particles in an electric field is directly connected with this stabilizing potential, so that these measurements give quantitative information in regard to the stability of the system. Kepfer and Walton (3) employed flocculation methods to follow the change in stability of their colloidal catalyst, ferric oxide. However, with colloidal platinum, in order to have the reaction slow enough to be measured accurately, the sol must be so dilute that flocculation values are not conveniently determined by macroscopic observation. In an effort to determine if the concentration of electrolyte corresponding to the flocculation value had any distinctive effect (as is the case with colloidal ferric oxide) on the velocity of decomposition of hydrogen peroxide, flocculation values were run on the concentrated sol. The migration velocity of the particles of the concentrated sol in the presence of the concentration of electrolyte corresponding to the flocculation values was then determined, using an ultramicroscopic method (5). The results are given in table 1 and show the close connection between the flocculation and migration methods as means of determining the stability of colloidal platinum.

TABLE 1

Relation between migration velocity and flocculation value (concentrated platinum sol)

ELECTROLYTE		BY OBSERVATION AFTER 16 HOURS	MIGRATION VELOCITY
	millimols per liter		*mu/sec /v /cm*
NaCl	0		−3 3
	1	Stable	
	2	Stable	−2 5
	3	Stable	
	4	Partially flocculated	−2 2
	5	Flocculated	−2 0
	10	Flocculated	
$BaCl_2$	0 05	Stable	
	0 06	Stable	−2 1
	0 08	Flocculated	−1 9
	0 10	Flocculated	
	0 20	Flocculated	
	0 50	Flocculated	
$AlCl_3$	0 004	Flocculated	
	0 006	Flocculated	
	0 01	Flocculated	
	0 02	Flocculated	
	0 04	Partially flocculated	+1 9
	0 06	Stable	+2 2
	0 08	Stable	

With both sodium chloride and barium chloride the migration velocity corresponding to the flocculation value is approximately −2 mu per second per volt per centimeter (the sol being negatively charged). This velocity corresponds to a "critical" potential of about 30 millivolts. In the case of aluminum chloride the smallest concentration used has already reduced the migration velocity below this critical value, and the sol was flocculated. With increasing concentration of aluminum chloride the colloidal platinum again became stabilized as a positively charged sol. This stabilization apparently took place when the positively charged colloidal particles had a migration velocity of about 2 mu per second per volt per centimeter. All the results obtained here not only agree with the postulate of Powis (6) that it is not necessary to deprive the particles of lyophobic colloids completely of their charge to cause flocculation, but also show that in order to have a stable platinum sol it is necessary to have sufficient electrolyte adsorbed to contribute a potential difference of over 30 millivolts.

The platinum sol was diluted to the concentration of the decomposition experiments and measurements of the migration velocity of the colloidal particles were taken over the same range of concentration with each of the electrolytes whose effect on the catalytic decomposition of hydrogen peroxide was studied. In this way the change in the migration velocity could be directly compared with the effect on the rate of decomposition of the hydrogen peroxide.

It has been concluded that at a migration velocity of −2 mu per second per volt per centimeter, the platinum sol enters a region of instability where it will flocculate on standing. It is evident from all of the curves that this point lies on a curve of increasing retardation but is of no unusual significance in the effect of the electrolyte on the catalytic decomposition of hydrogen peroxide.

EXPERIMENTAL RESULTS

The decomposition of hydrogen peroxide as catalyzed by colloidal platinum was studied in the presence of both the chlorides and nitrates of sodium, aluminum, and thorium, and in the presence of barium chloride. The change in migration velocity of the same concentration of platinum sol in conductivity water, with addition of the above salts, was also determined. The results are tabulated below in tables 2 to 5, and represented graphically in the accompanying figures 1 to 5. In the figures the concentration of electrolyte in millimols per liter is plotted against the time for 50 per cent decomposition in the case of hydrogen peroxide decomposition, and against mu per second per volt per centimeter in the case of the migration velocity of the colloidal particles in an electric field.

Effect of sodium salts

The first experiments on the effect of electrolytes on the catalysis were made with a univalent ion, sodium. Data (table 2) were obtained for both sodium chloride and sodium nitrate. The effects of sodium nitrate and sodium chloride on the rate of decomposition of the hydrogen peroxide are illustrated in figures 1 and 2, respectively, where they are compared with the effects of the same salts on the migration velocity of the colloidal particles. It is evident that up to a certain point these two effects correspond rather closely, and it may be deduced that within this concentration range the effect is similar to that found by Kepfer and Walton for

TABLE 2

Effect of sodium salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

ELECTROLYTE		AVERAGE 0 4343*K*	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
	millimols per liter		*minutes*	*mu/sec /v /cm.*
NaCl	0	0 01258	24	−2 8
	1			−2 1
	2 63	0 00512	58 8	−2 0
	5			−1 7
	6 58	0 00398	75 7	−1 7
	9 9	0 00367	82 1	−1 6
	13 2	0 00333	90 5	−1 6
	17 1	0 00291	104	−1 6
	21 1	0 00248	121	−1 6
	26 3	0 00210	143	−1 6
	50			−1 5
NaNO$_3$	0	0 01046	28 8	−2 8
	1 31	0 00491	61 4	−2 1
	2 63	0 00465	64 7	−1 8
	5 26	0 00436	69 0	−1 6
	10 5	0 00452	66 6	−1 4
	13 2	0 00448	67 2	−1 4
	17 1	0 00432	69 7	−1 4
	21 1	0 00410	73 5	−1 4
	26 3	0 00366	82 3	

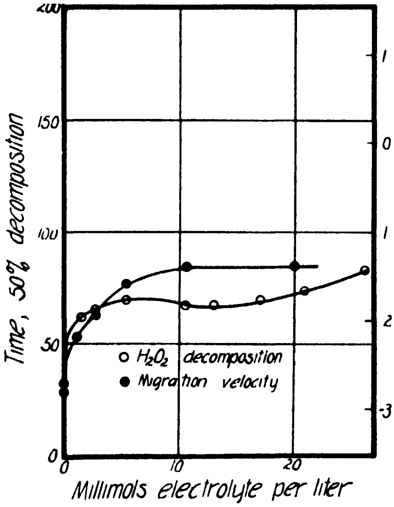

FIG. 1

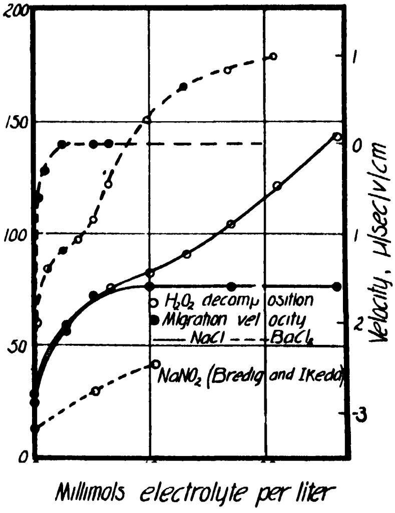

FIG. 2

FIG. 1. SODIUM NITRATE

FIG. 2. SODIUM CHLORIDE AND BARIUM CHLORIDE

colloidal ferric oxide, and that the hydrogen peroxide decomposition is decreased or retarded because of modifications in the surface ionization of the colloid.

With concentrations of sodium salts greater than 7 or 8 millimols per liter there is very little further change in the migration velocity of the colloidal particles. In the presence of sodium chloride, however, the retardation of the hydrogen peroxide decomposition continues to increase in practically a straight-line relationship. With sodium nitrate the retarding effect increases very little. This latter effect on the decomposition is, then, apparently due to the anion of the electrolyte added.

TABLE 3

Effect of barium chloride on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

BARIUM CHLORIDE	AVERAGE 0.4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
millimols per liter		*minutes*	*mu/sec /v./cm.*
0	0.01249	24.1	−2.8
0.025			−2.5
0.03			−2.1
0.04			−1.9
0.05			−1.5
0.10			−1.2
0.50			−0.6
1.0			−0.3
1.32	0.00358	84.2	Isoelectric
2.63	0.00326	92.4	Isoelectric
3.95	0.00310	97.1	Isoelectric
5.26	0.00283	106	Isoelectric
6.58	0.00248	122	
9.9	0.00200	151	
13.2	0.00181	166	
17.1	0.00174	173	
21.1	0.00169	179	

Effect of barium chloride

The effect of this bivalent chloride is similar to that of sodium chloride. The results are given in table 3 and figure 2. Barium ions are more strongly adsorbed than sodium ions, and the retarding of the rate of decomposition of hydrogen peroxide is consequently greater. Below a concentration of about 4 millimols of barium chloride per liter the curves for hydrogen peroxide decomposition and migration velocity distinctly show that there is a connection between the two effects. At higher concentrations the colloidal particles are isoelectric, but the same further retarding of the catalysis of the hydrogen peroxide decomposition that was obtained with sodium chloride is evident here; the retarding effect decreases, however, at the higher concentrations.

Effect of aluminum salts

The effect of neutral univalent and bivalent salts has been shown. Since the salts of all trivalent and tetravalent metals are hydrolyzed in solution it was not possible to compare them directly with the neutral salts A change in pH of the solution would presumably introduce complications. Even so, the effect of these salts on the catalysis was of interest. Aluminum was chosen as a typical trivalent metal, and experiments were made using both aluminum chloride and aluminum nitrate (table 4 and figures

TABLE 4

Effect of aluminum salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

ELECTROLYTE		AVERAGE 0 4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
	millimols per liter		*minutes*	*mu/sec /v /cm*
$AlCl_3$	0	0 01236	24 3	−2 8
	0 002			+1 1
	0 004			1 3
	0 011	0 00337	89 4	2 2
	0 021	0 00314	95 9	2 8
	0 029	0 00258	117	3 4
	0 040	0 00303	99 4	3 3
	0 050	0 00310	96 7	2 8
	0 066	0 00304	99 0	2 9
	0 105	0 00257	117	3 0
	0 158	0 00240	125	3 4
	0 237	0 00222	136	3 1
	0 316	0 00210	144	2 7
	0 526	0 00189	159	2 5
	0 79	0 00169	178	2 5
	3 95	0 00076	396	2 5
	6 58	0 00059	510	2 4
$Al(NO_3)_3$	0 005	0 00335	89 9	
	0 011	0 00327	92 1	2 6
	0 040			3 9
	0 053	0 00295	102	3 8
	0 105	0 00322	93 4	3 1
	0 12			2 8
	0 158	0 00404	74 5	3 1
	0 211	0 00363	82 9	2 9
	0 368	0 00400	75 3	2 6
	0 526	0 00415	72 6	2 6
	0 79	0 00437	68 8	2 6

3 and 4). These salts are apparently about equally hydrolyzed, the pH of $M/1000$ aluminum chloride being 3.6 and of $M/1000$ aluminum nitrate 3.7. Any difference, in their effect, therefore, should not be due to a difference in acidity.

As expected, the aluminum salts are effective in a much lower concentration range than sodium or barium salts. At the lower concentrations the courses of the curves, represented in figures 3 and 4, are peculiar, and are probably affected by the operation of several factors, such as adsorption, ion exchange, and hydrolysis. It is to be noted, however, that in general the same kind of change in the first part of the curves is shown both in the rate of hydrogen peroxide decomposition and in the migration velocity.

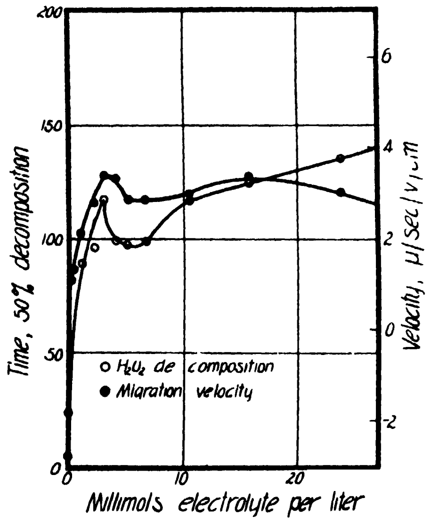

FIG. 3. ALUMINUM CHLORIDE

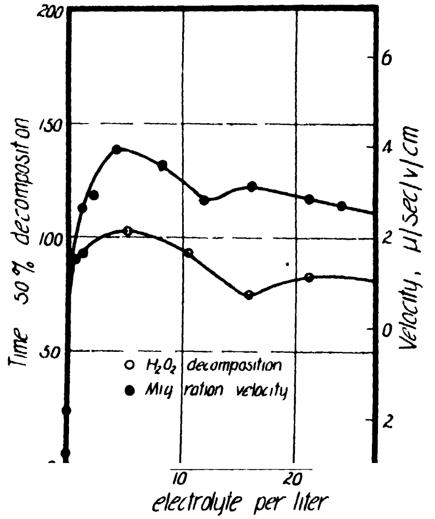

FIG 4 ALUMINUM NITRATE

Aluminum ions are so strongly adsorbed that the colloidal system is stable as a positively charged sol during almost the entire range of concentration measured here. The slower rate of decomposition of this positively charged sol demonstrates that it is the condition of the colloid surface rather than its stability which is most important in catalyzing the decomposition of hydrogen peroxide.

At higher concentrations the same difference between the effect of aluminum chloride and aluminum nitrate on the rate of hydrogen peroxide decomposition is shown that was obtained with sodium chloride and sodium nitrate. The effect of aluminum nitrate on the decomposition velocity follows the migration velocity curve rather closely throughout the whole range of concentration measured here. With aluminum chloride the retarding effect follows the change in migration velocity only in the first part of the curve, and then shows a continual increase which apparently has no connection with the change in migration velocity. As can be seen from the data in table 4, the retarding effect is still increasing at higher concentrations than are shown in figure 3.

Effect of thorium salts

Results of experiments with the tetravalent salts, thorium chloride and thorium nitrate, are given in table 5 and figure 5.

TABLE 5

Effect of thorium salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

THORIUM SALTS		AVERAGE 0.4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
millimols per liter			*minutes*	*mu/sec/v/cm*
$ThCl_4$	0	0.01216	24.8	−2.6
	0.026	0.00654	46.1	+4.8
	0.053	0.00540	55.9	4.6
	0.079	0.00468	64.4	4.5
	0.158	0.00333	90.4	4.2
	0.237	0.00251	120	4.2
	0.368	0.00200	151	4.1
	0.526	0.00155	194	4.1
	1.0			3.8
$Th(NO_3)_4$	0	0.01216	24.8	−2.6
	0.011	0.01138	26.5	
	0.026	0.01093	27.6	+3.9
	0.040	0.01309	23.0	3.9
	0.053	0.01457	20.7	3.9
	0.079	0.01471	20.5	3.8
	0.105	0.01444	20.8	3.8
	0.290	0.01579	19.1	3.4
	0.526	0.01653	18.3	3.4
	1.0			3.4

The effect of thorium salts on the catalytic decomposition of hydrogen peroxide does not show the close relation to their effect on the migration velocity of the colloidal particles that characterizes aluminum salts. Thorium ions have a greater effect on the migration velocity than aluminum ions, but this may be due to the greater valence of the thorium ion, and aluminum ions may actually be more strongly adsorbed on the colloid surface, thus exerting a greater retardation on the catalysis. Thorium ions should, nevertheless, show some retarding effect and, since thorium nitrate has little or none, it would seem advisable to look for further explanation. Any thorium hydroxide formed by hydrolysis does not directly decompose hydrogen peroxide, or only does so very slowly, for thorium salts alone, in the concentrations used, had a negligible effect on the hydrogen peroxide. However, it is possible that the tendency of thorium hydroxide to combine with hydrogen peroxide (7) greatly decreases the adsorption of thorium ions by the colloidal platinum. This tying up of thorium ions would not be indicated in the migration velocity measurements obtained here, since, on account of the experimental difficulties involved by the evolution of oxygen bubbles, they were not made in the presence of hydrogen peroxide.

If such a reaction is a factor, allowing the thorium salt to act on the colloidal platinum before it comes in contact with the hydrogen peroxide should give a greater retardation of the rate of decomposition. An experiment was therefore carried out in which the electrolyte was first added to the platinum sol, and the hydrogen peroxide added last. The data are given in table 6.

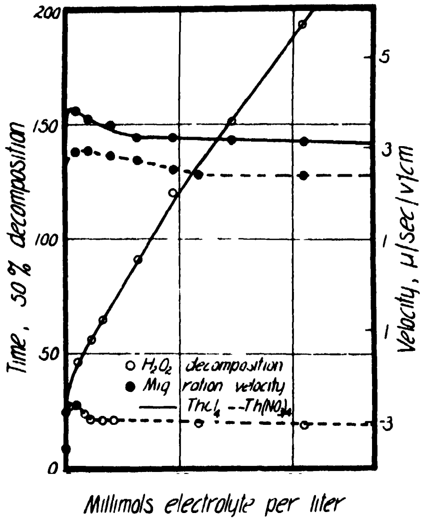

FIG. 5. THORIUM CHLORIDE AND THORIUM NITRATE

The time for 50 per cent decomposition of about 50 minutes corresponds to a 50 per cent decomposition in 20.8 minutes when the electrolyte was added to the hydrogen peroxide first. The "constants" calculated for a unimolecular reaction increase very rapidly; the constant for a zero order reaction, calculated in the last column, is much more applicable. With sodium nitrate, on changing the order of mixing in the same way, there was no difference either in the time for 50 per cent decomposition or in the velocity constant.

The results obtained in this experiment with thorium nitrate might be interpreted to indicate that the hydrogen peroxide is more strongly adsorbed under these conditions, while at the same time the rate of reaction is decreased. The rate of reaction has decreased, presumably, because the thorium salt has affected the colloidal surface. An attraction between thorium and hydrogen peroxide might, however, serve to attract the hydrogen peroxide more strongly to the surface of the platinum on which the thorium ions were adsorbed, and consequently give a change in the order of the reaction, such as was obtained here. However, the data are inadequate for any conclusions at this time.

Pennycuick (8) has found anomalous results for ferric chloride compared to aluminum salts in his study of the effect of electrolytes on colloidal platinum. He ascribes this to the much higher degree of hydrolysis of ferric chloride, so that the hydrogen ions are of primary importance rather than the extremely low concentration of ferric ions. Thorium salts are also highly hydrolyzed in solution, as the following data (9) indicate:

TABLE 6

Results obtained when thorium nitrate acts on colloidal platinum before it comes in contact with hydrogen peroxide

0.105 Millimols of thorium nitrate per liter

TIME	TITRATION	DECOMPOSED	$0.4343K_1$	K_0
minutes		*per cent*		
0	49.75	0		
15	42.15	15.28	0.00480	0.01019
30	34.15	31.36	0.00545	0.01045
45	26.65	46.43	0.00602	0.01032
60	20.00	59.80	0.00660	0.00997
75	14.70	70.45	0.00706	0.00939
90	10.95	77.99	0.00730	0.00867
Average			0.00621	0.00983
Time for 50 per cent decomposition			48.5 minutes	50.9 minutes

M/1000 solutions	*pH (glass electrode)*
$AlCl_3$	3.6
$CrCl_3$	2.8
$FeCl_3$	2.3
$ThCl_4$	2.7

The other evidence, particularly the migration velocities, does not indicate, however, that the effect of thorium salts as studied here can be considered as primarily that of the hydrogen ion.

Aside from the effect of the thorium ion, it is seen from figure 5 that thorium salts show even more distinctly than those of sodium and aluminum the difference between the effect of nitrates and chlorides on the catalytic decomposition of hydrogen peroxide by colloidal platinum.

DISCUSSION

Of the results which have been obtained here on the effect of electrolytes on the catalysis, the most striking feature is the very wide difference between the effect of chlorides and nitrates at the higher concentrations. While this might be due to the formation of free chlorine, with subsequent alteration of the catalyst surface, it is the opinion of the authors that in the concentrations used such an effect would be very small. Another explanation of this difference may involve the structure of colloidal platinum, and the mechanism of the decomposition reaction. The constitution of colloidal platinum has been the subject of thorough investigation by Pennycuick (10). He gives as the simplest formula for the sol: $(x\mathrm{Pt} \cdot y\mathrm{PtO_2} \cdot z\mathrm{Pt(OH)_6})2z^- \ldots . 2z\mathrm{H}^+$, Pt conventionally representing the interior of the particle, PtO_2 the oxide which covers the surface, and $Pt(OH)_6^=$ the stabilizing surface ionogen which is combined with part of the surface oxide, some evidence suggesting that it is bound at the surface only at active points. The weakly acidic surface oxide is converted by bases into more surface ionogens, which accounts for the protective action of univalent bases on colloidal platinum.

It has been shown by Bredig and others that the addition of a univalent base increases the rate of decomposition of hydrogen peroxide by colloidal platinum, up to a certain optimum concentration. Therefore, if Pennycuick is correct and the stabilizing effect of bases is due to the formation of more of the ionizing salt, there is apparently a close connection between the amount of this complex ion which is present on the active points of the surface and the catalytic activity of the colloid in decomposing hydrogen peroxide. It may be postulated that the decomposition of the hydrogen peroxide is actually effected by this complex in some such way as the following:

$$\left\{\begin{matrix} \mathrm{HO} & & \mathrm{OH} \\ \mathrm{HO} & \mathrm{Pt} & \mathrm{OH} \\ \mathrm{HO} & & \mathrm{OH} \end{matrix}\right\}^{=} + \mathrm{H_2O_2} = \left\{\begin{matrix} \mathrm{HO} & & \mathrm{OH} \\ & \mathrm{Pt} & \\ \mathrm{HO} & & \mathrm{OH} \end{matrix}\right\}^{=} + 2\mathrm{H_2O} + \mathrm{O_2}$$

The first step may be the formation of an unstable intermediate adsorption complex, decomposing into the above indicated products. The platinous acid may again be oxidized by hydrogen peroxide:

$$\left\{\begin{matrix} \mathrm{HO} & & \mathrm{OH} \\ & \mathrm{Pt} & \\ \mathrm{HO} & & \mathrm{OH} \end{matrix}\right\}^{=} + \mathrm{H_2O_2} = \left\{\begin{matrix} \mathrm{HO} & & \mathrm{OH} \\ \mathrm{HO} & \mathrm{Pt} & \mathrm{OH} \\ \mathrm{HO} & & \mathrm{OH} \end{matrix}\right\}^{=}$$

Replacement of hydroxyl radicals by other groups would destroy the effectiveness of the catalyst. Pennycuick (11) has shown that hydrocyanic acid, in the same way as bases, is removed from solution by the colloid and reacts with the weakly acidic surface oxide to produce more surface ionogens of the form $[PtO_2CN]^-$ or $[Pt(CN)_6]^=$. Unlike the univalent bases, however, hydrogen cyanide is a poison for the catalytic property of colloidal platinum. This would be expected because the ionogens now contain cyanide instead of hydroxyl radicals.

The substitution of chloride for hydroxyl in this complex would explain the retarding effect of chlorides at higher concentrations, as was found here. Since the nitrates do not easily form complex compounds in which several NO_3^- residues group themselves around a metal atom (12), the addition of nitrates should not show this retarding effect; this has been found to be true.

The fluoride ion would be expected to be inactive, since it also does not readily form complexes with such metals as platinum (13). Kastle and Loevenhart (14), studying the effect of the alkali halides, found that the fluoride did not inhibit the catalytic decomposition of hydrogen peroxide by colloidal platinum. NO_2^- residues, however, should replace the hydroxyls rather readily, and a retarding effect would be expected. Bredig and Ikeda (15) have studied the effect of sodium nitrite on the catalytic decomposition of hydrogen peroxide by colloidal platinum. Their results are plotted on figure 1 and show a considerable retarding of the catalysis.

The catalytic activity of hexahydroxyplatinic acid seems to depend on its being attached to active points of the colloid. A solution of hexahydroxyplatinic acid showed no catalytic activity, and adding hexahydroxyplatinic acid only slightly increased the activity of colloidal platinum.

The effect of salts of four different metals on the catalytic decomposition of hydrogen peroxide by colloidal platinum is, with some exceptions, very similar. The first result is a retarding of the catalysis, which follows very closely the effect of the electrolyte on the stability of the colloidal system, and which can be attributed to modifications in the colloid surface and in the ionization of the stabilizing surface complexes. This effect is practically the same as that which Kepfer and Walton have found for comparable electrolytes on the catalytic decomposition of hydrogen peroxide by colloidal ferric oxide. Thus for two different colloidal catalysts one important effect of the addition of electrolytes is to so modify the surface of the colloid that the adsorption of hydrogen peroxide is reduced and the rate of decomposition retarded.

In the case of colloidal platinum there is then a further effect due to the substitution of certain anions in the surface complex (principally $Pt(OH)_6^=$), which prevents or retards the chemical reaction by which the hydrogen peroxide is decomposed. Salts whose anions are not easily substituted in the surface complex do not show this further retarding effect.

SUMMARY

1. The catalytic decomposition of hydrogen peroxide by colloidal platinum has been investigated at a temperature of 25°C. The effect of additions of sodium chloride, barium chloride, aluminum chloride, thorium chloride, sodium nitrate, aluminum nitrate, and thorium nitrate has been studied over a considerable range of concentration, and compared with their effect on the migration velocity of the colloidal platinum particles in an electric field. A relation between the change in the rate of decomposition of hydrogen peroxide and the migration velocity of the colloidal particles has been shown.

2. Thorium salts do not show as close a relation between migration velocity of the colloidal particles and effect on the catalytic decomposition of hydrogen peroxide.

3. Evidence of a further effect of anions on the catalytic decomposition of hydrogen peroxide by colloidal platinum has been found, and a possible explanation based on substitution in the Werner complex of hexahydroxyplatinic acid on the colloid surface is advanced. The nitrate ion, which is not readily substituted in the complex, does not show this effect.

A possible mechanism for the reaction involving hydrogen peroxide and hexahydroxyplatinic acid is given.

REFERENCES

(1) Bredig and v. Berneck, Müller: Z. physik. Chem. **31**, 258 (1899).
Bredig and Ikeda: Z. physik. Chem. **37**, 1 (1901).
Bredig and Fortner: Ber. **37**, 798 (1904).
Bredig and Reinders: Z. physik. Chem. **37**, 323 (1901).
Brossa: Z. physik. Chem. **66**, 162 (1909).
McIntosh: J. Phys. Chem. **6**, 15 (1902).
Price and Denning: Z. physik. Chem. **46**, 89 (1904).
Kastle and Loevenhart: Am. Chem. J. **29**, 397, 563 (1903).
(2) Lottermoser and Lehmann: Kolloid Z. **29**, 250 (1921).
(3) Kepfer and Walton: J. Phys. Chem. **35**, 557 (1931).
(4) Bredig and v. Berneck, Müller: See reference 1.
Bredig and Ikeda: See reference 1.
(5) Hazel and Ayres: J. Phys. Chem. **35**, 2930 (1931).
(6) Powis: Z. physik. Chem. **89**, 186 (1915).
(7) Pissarjewsky: Z. anorg. Chem. **25**, 388 (1900); **31**, 359 (1902).
(8) Pennycuick: J. Chem. Soc. **1929**, 618.
(9) Data furnished by Dr. Fred Hazel, University of Wisconsin.
(10) Pennycuick: J. Am. Chem. Soc. **52**, 4621 (1930); J. Chem. Soc. **1928**, 2108; Kolloid Z. **49**, 407 (1929); J. Chem. Soc. **1929**, 618, 623.
(11) Pennycuick: J. Am. Chem. Soc. **52**, 4628 (1930).
(12) Ephraim: Inorganic Chemistry, p. 594. Gurney and Jackson, London (1926).
(13) Latimer and Hildebrand: Reference Book of Inorganic Chemistry, p. 77. The MacMillan Company, New York (1929).
(14) Kastle and Loevenhart: Am. Chem. J. **29**, 412 (1903).
(15) Bredig and Ikeda: Z. physik. Chem. **37**, 49 (1901).

A RULE FOR THE EXPRESSION OF THE PARTITION OF ASSOCIATING SUBSTANCES

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The distribution of associating substances between water and various other solvents usually has been expressed by some form of the empirical equation,

$$C_x/C_w^a = K$$

where C_x represents the molar concentration of the distributed substance in the non-aqueous layer and C_w the concentration in the aqueous layer. Since the exponent of the concentration in water is not a whole number, it has little real meaning.

When distributed between water and another solvent, such as benzene or chloroform, associating substances give apparent distribution ratios with a relation to the concentration in the aqueous phase that may be expressed accurately by the equation,

$$\text{Apparent distribution ratio} = C_x/C_w = K_s\, C_w + K_i$$

The equation is that for a straight line with a slope, K_s, and an intercept, K_i. C_x and C_w refer to concentrations in moles per liter, irrespective of association or dissociation.

In figure 1 are shown a few examples of apparent distribution ratios, C_x/C_w, plotted against C_w. The data used are given by the International Critical Tables (1) and by Smith and White (2). The equation holds quite well at moderate values of C_w, as may be seen from the figure, and provides a simple means of recording and testing the experimental data. It also makes interpolation and extrapolation easier.

A similar equation may be derived upon making a few assumptions. Taking A and A_n to represent the single and the associated molecules in the y phase, respectively, and A' and A_n' to represent the single and the associated molecules in the x phase, respectively, one may construct the following equations, according to the mass law.

$$nA \rightleftharpoons A_n \qquad K_1 = (A_n)/(A)^n$$

$$A \rightleftharpoons A' \qquad K_2 = (A')/(A)$$

$$nA' \rightleftharpoons A'_n \qquad K_3 = (A'_n)/(A')^n$$

$$C_x = n\ (A'_n) + (A')$$

$$C_y = n\ (A_n) + (A)$$

C_x and C_y may both be expressed in terms of (A) and the constants, hence,

$$C_x = nK_3K_2^n(A)^n + K_2(A)$$

$$C_y = nK_1(A)^n + (A)$$

and,

$$C_x/C_y \quad \frac{nK_3K_2^n(A)^{n-1} + K_2}{nK_1(A)^{n-1} + 1}$$

It is broadly established that associating substances give little or no evidence of association in water at moderate concentrations. It may be assumed, therefore, that in water the quantity, $nK_1(A)^{n-1}$, is negligible with respect to 1 and that (A) is practically equal to C_w. The equation then takes the simpler form,

$$C_x/C_w = nK_3K_2^nC_w^{n-1} + K_2$$

When the distribution ratio is a linear function of C_w, it is evident that n equals the whole number 2, and that two molecules are associated in the non-aqueous phase. In this case the equation reduces to a form similar to that of the experimental equation, namely,

$$C_x/C_u = 2K_3K_2^2C_w + K_2$$

It is of interest to mention one example, that of the partition of formaldehyde between water and chloroform, in which the equation fits the data very well when n is taken equal to 3. The tendency of the aldehydes to form trimers is well known.

Values for K_2, the distribution constant for single molecules, and for K_3, the association constant in the non-aqueous phase, may be calculated. K_2 may be taken equal to K_i, the intercept of the experimental equation. K_3 may be found by taking the quantity, $2K_3K_2^2$, equal to the experimental slope, K_s, and solving. In this way have been obtained the values for K_2 and K_3 given in table 1. Hendrixson (3) has calculated some similar constants for benzoic acid, and Smith and White (2) have calculated constants for a number of organic acids by other methods. The distribution constants obtained in the above manner from the data of Smith and White on propionic and isobutyric acid are practically equal to the constants calcu-

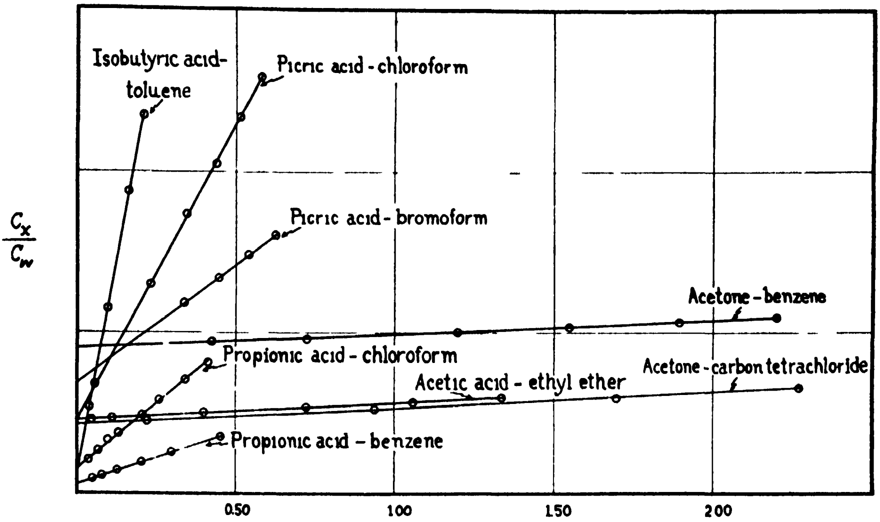

Fig 1. The Relation of the Apparent Distribution Ratio, C_x / C_w, to the Concentration in Water, C_w, of a Number of Associating Substances Distributed Between Water and Other Solvents as Indicated, at 25°C.

TABLE 1

Distribution and association constants calculated from partition data at 25°C.

DISTRIBUTED SUBSTANCE	NON-AQUEOUS SOLVENT	DISTRIBUTION CONSTANT K_2	ASSOCIATION CONSTANT K_3
Acetic acid	Benzene	0.0106	108
	Chloroform	0.065	4.1
	Ethyl ether	0.46	0.24
Acetone	Carbon tetrachloride	0.43	0.28
	Benzene	0.91	0.050
Picric acid	Chloroform	0.46	8.6
	Bromoform	0.68	1.6
Lactic acid	Ethyl ether	0.081	0.97
Isobutyric acid	Toluene	0.138	281
	Benzene	0.180	201
	Chloroform	0.56	54
Propionic acid	Toluene	0.046	134
	Benzene	0.063	78.5
	Chloroform	0.164	30.0

lated by these authors. Their association constants are in error throughout by a factor of 2, but otherwise agree well with the reciprocal of K_3.

The simple equation is valid over what may be considered a significant and useful range of concentrations. A multitude of factors, however, may cause a departure from the equation. At very low concentrations, certain classes of substances undergo electrolytic dissociation which becomes sufficient to cause a noticeable lowering of the ratio, C_x/C_w, but may be taken into account when the dissociation constants are known. At high concentrations, on the other hand, association in the aqueous phase must increase to an important extent, also exerting a lowering influence on the ratio.

The solvents are at all times saturated with each other. In addition, their mutual solubility increases with increasing concentrations of the dissolved substance until, in many cases, the system becomes a single phase. These effects greatly hinder a correlation of partition data with that secured from studies of freezing point lowering, partial pressures, etc., in unmixed solvents. Saturation of either phase with the distributed substance causes a failure of all partition laws.

In developing the equation for the apparent distribution ratio it was assumed that n is the same in both solvents. It cannot be proven, at present, that this is the case, or that only one value of n exists in any one solvent, or that for any one value of n the molecules associate always in the same way.

REFERENCES

(1) International Critical Tables, Vol. III, pp. 422–33. McGraw-Hill Book Co., New York (1928)
(2) SMITH AND WHITE: J. Phys. Chem. **33**, 1953 (1929).
(3) HENDRIXSON: Z. anorg Chem. **13**, 73 (1897).

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SIMPLIFIED FORMULAS FOR THE CALCULATION OF EXPANSION COEFFICIENTS AND COMPRESSIBILITIES OF GASES AT LOW PRESSURES FROM THE BEATTIE-BRIDGEMAN EQUATION OF STATE

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J. A. Beattie and O. C. Bridgeman (1) have developed an equation of state that relates p, V, and T in a simple form involving only five constants, each set of constants being specific to a gas in addition to the gas constant R. The equation may be written in the virial form in terms of either p or V and is expressed:

$$p = \frac{nRT}{V} + \frac{n^2\beta}{V^2} + \frac{n^3\gamma}{V^3} + \frac{n^4\delta}{V^4} \tag{1}$$

where

$$\beta = RTB_0 - A_0 - Rc/T^2 \tag{2}$$

$$\gamma = -RTB_0b + A_0a - RB_0c/T^2 \tag{3}$$

$$\delta = RB_0bc/T^2 \tag{4}$$

A_0, a, B_0, b, and c are the characteristic constants for each gas.

From equation 1 Beattie (2) derives the value of V in terms of p and obtains:

$$V = \frac{nRT}{P} + \frac{n\beta}{RT} + \frac{n\gamma}{R^2T^2} \cdot p + \frac{n\delta}{R^3T^3} \cdot p^2 \tag{5}$$

It will be observed from an examination of the equations as written in the virial forms that the values of p or V at 0°C. and 100°C. may be calculated by insertion of the correct values of β, γ, δ, the values of these coefficients at the two temperatures stated being calculated from equations 2, 3, and 4.

Values of the five constants for thirteen gases have been conveniently tabulated (3) and from these values β_1 and γ_1 at 100°C. have been calculated, the values of the virial coefficients at 0°C. having been obtained from computations made by Beattie and Bridgeman.

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From a knowledge of these values it is possible to calculate the coefficients of expansion at constant pressure (α_v) and constant volume (α_p), for

$$\alpha_v = \frac{1}{v_0}\left[\frac{dv}{dt}\right]_{p\,=\,\mathrm{const}}$$

$$\alpha_p = \frac{1}{p_0}\left[\frac{dp}{dt}\right]_{t\,=\,\mathrm{const}}$$

where v_0, p_0 represent the volume or pressure of the gas at 0°C. and $\frac{dv}{dt}$, $\frac{dp}{dt}$ the rate of increase of volume or pressure with temperature.

The values of α_v, α_p, here derived are for the temperature interval 0°C. to 100°C. and at a constant pressure of 1 atmosphere in the first case and an initial pressure of 1 atmosphere in the second case.

If we consider 1 gram-molecule of gas (that is, $n = 1$) then we have from equation 1

$$p_0 = \frac{RT_0}{V} + \frac{\beta_0}{V^2} + \frac{\gamma_0}{V^3} \quad \text{at } 0°\text{C}$$

$$p_1 = \frac{RT_1}{V} + \frac{\beta_1}{V^2} + \frac{\gamma_1}{V^3} \quad \text{at } t°\text{C}.$$

and from equation 5 when the pressure is 1 atmosphere we have:

$$V_0 = RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^2} \quad \text{at } 0°\text{C}.$$

$$V_1 = RT_1 + \frac{\beta_1}{RT_1} + \frac{\gamma_1}{R^2T_1^2} \quad \text{at } t°\text{C}.$$

Taking as our units those cited by Beattie and Bridgeman, i.e., moles, liters, atmospheres and ° Kelvin, we may calculate values of α_v at a constant pressure of 1 atmosphere and α_p at an initial pressure of 1 atmosphere over the range 0°C. to 100°C. from the following equations:

$$\alpha_v = \frac{\left[RT_1 + \frac{\beta_1}{RT_1} + \frac{\gamma_1}{R^2T_1^2}\right] - \left[RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^2}\right]}{\left[RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^2}\right] \cdot 100}$$

where $p = 1$ atmosphere, $T_0 = 273.13$°C., $T_1 = 373.13$°C., and

$$\alpha_p = \frac{\left[RT_1 + \frac{\beta_1}{V} + \frac{\gamma_1}{V^2}\right] - \left[RT_0 + \frac{\beta_0}{V} + \frac{\gamma_0}{V^2}\right]}{\left[RT_0 + \frac{\beta_0}{V} + \frac{\gamma_0}{V^2}\right] \cdot 100}$$

where V = const. = 22.4131 liters at N.T.P.

Substituting values of β which contribute the major portion to the divergence from the perfect gas law, and values of γ which contribute about 1 in 15,000 as a maximum to the value of the coefficient, we arrive at the values given in table 1, which are compared with those calculated by Leduc (4) and those determined experimentally. The experimental figures have been taken from the International Critical Tables, and where necessary the values at 1 atmosphere have been interpolated from the data given. Values not obtained from the International Critical Tables have a definite reference given.

It may be claimed that the performance of the equation is extremely good: it shows clearly the phenomenon that α_p for hydrogen, nitrogen, and helium is greater than α_v. The values for nitrogen, oxygen, and air are certainly reliable and that for carbon dioxide agrees well with the predictions of Leduc and the experimental figure. The values for methane are a little unsatisfactory and those for ethylene are disappointingly low compared with the calculations of Leduc; investigation into this point seems desirable. For ammonia the predictions are satisfactory in the case of the pressure coefficient, the value calculated agreeing almost exactly with that experimentally observed, but it seems curious that the value of α_v shows such a discrepancy It would appear that values of the volume coefficient are more susceptible to external factors, such as the increase in volume caused by the evolution of adsorbed layers from the surface of the

TABLE 1

	COEFFICIENTS* AT CONSTANT PRESSURE			COEFFICIENTS AT CONSTANT VOLUME		
	α_v (calculated)	Leduc (calculated)	Experimental	α_p (calculated)	Leduc (calculated)	Experimental
He	3659 1	—	3659	3661 3	—	3661
Ne	3660 6	–	3660^5	3662 8	—	3661^5
A	3672 4	–	3673	3671 7	—	3672
H_2	3660 3	3662	3660	3662 7	3664	3662
N_2	3670 9	3671	3670 5	3671 8	3672	3671 5
O_2	3674 6	3673	3674	3673 5	3672	3674
Air	3671 1	—	3671	3671 6	–	3672
CO_2	3721 7	3723	3723	3710 0	3712	3712
CH_4	3689 4	3681	3683	3688 1	3678	3680
C_2H_4	3724 2	3735		3710 5	3722	—
NH_3	3790 0	380	3847^6	3767 8	377	3769^6
CO	3670 9	3672	3669^7	3671 8	3673	3668^7
N_2O	3721 7	3732	3720^7	3710 0	3719	—

* All these coefficients have been multiplied by 10^6 except Leduc's figures for ammonia, which are multiplied by 10^5.

containing vessels with rise in temperature and thereby vitiating the true values of the increase of volume with temperature.

The values for carbon monoxide and nitrous oxide are assumed by Beattie and Bridgeman (8) to be the same as those for nitrogen and carbon dioxide. This assumption seems fully justified in the case of carbon monoxide, but for nitrous oxide this is probably not quite true, as shown by the divergence between the predicted values of Leduc and those calculated from the Beattie constants for carbon dioxide.

The compressibility of a gas is given by the equation

$$1+\lambda=\frac{p_0v_0}{p_1v_1}$$

at constant temperature, where p_0v_0 is the product at zero pressure and p_1v_1 the product at 1 atmosphere.

From the Beattie-Bridgeman equation of state we have at any temperature, T_1,

$$(1+\lambda)_{T_1}=\frac{RT_1}{RT_1\left(1+\frac{\beta_1}{RT_1V_1}\right)}$$

for

$$p_1V_1=RT_1+\frac{\beta_1}{V_1}$$

where V_1 is the corresponding volume of 1 gram-molecule at T_1° Absolute and β_1 is of the appropriate value. The omission of the further terms in the Beattie equation is justifiable at low pressures in this case, as values of $\frac{\gamma_1}{V^2}$ only contribute about 1 part in 100,000 to the final result.

As

$$V_1=RT_1+\frac{\beta_1}{RT_1}\ \text{(approximately)}$$

then

$$(1+\lambda)_{T_1}=1-\frac{\beta_1}{RT_1\left[RT_1+\frac{\beta}{RT_1}\right]}=1-\frac{\beta_1}{R^2T_1^2+\beta_1}$$

This simple form of equation allows the compressibilities of any gas to be calculated extremely rapidly over a wide temperature range, and in the case of the more compressible gases, such as carbon dioxide, the error involved is not greater than 1 part in 10,000. The agreement between the theoretical derivation of $1 + \lambda$ for temperatures between −100°C. and +100°C. and the experimental figures of Holburn and Otto (9) for nitrogen is satisfactory; and the assumption of Beattie and Bridgeman previously mentioned as regards the similarity of carbon monoxide and nitrogen seems fully borne out in the comparison of the values obtained from the data of Bartlett and his coworkers (10) on carbon monoxide and those calculated for nitrogen.

In table 2 the values $(1 + \lambda)_A$ are those calculated from the Beattie constants for nitrogen and those from Smith and Taylor's data (1) are given in the column designated $(1 + \lambda)_B$. $(1 + \lambda)_C$ values are the experimental determinations of Holborn and Otto for nitrogen, and the values given for $(1 + \lambda)_D$ are the figures obtained by Bartlett and coworkers for carbon monoxide.

TABLE 2

t°C.	$(1 + \lambda)_A$	$(1 + \lambda)_B$	$(1 + \lambda)_C$	$(1 + \lambda)_D$
−100	1 00369		1 00367	—
−50	1 00146	-	1 00144	1 00135
−25	1 00090	1 00082	—	1 00077
0	1 00051	1 00047	1 00046	1 00040
+25	1 00025	1 00024	1 00020	1 00018
+50	1 00006	1 00006	1 00000	1 00008
+100	0 99979	—	0 99980	0 99978

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REFERENCES

(1) Beattie and Bridgeman: Proc. Am. Acad. Arts. Sci. **63**, 229 (1928); J. Am. Chem. Soc. **49**, 1665 (1927), **50**, 3133 (1928).
(2) Beattie: Proc. Nat. Acad. Sci. **16**, 14 (1930).
(3) Beattie and Bridgeman: Z. Physik **62**, 95 (1930).
(4) Leduc: Ann. phys. **5**, 180 (1916).
(5) Heuse: Ann. Physik [5] **4**, 778 (1930).
(6) Perman and Davies: Proc. Roy. Soc. London **A78**, 28 (1906).
(7) Regnault: Ann. chim. phys. **4**, 5 (1842); **5**, 52 (1842).
(8) Beattie and Bridgeman: J. Am. Chem. Soc. **50**, 3151 (1928).
(9) Holborn and Otto: Z. Physik. **33**, 1 (1925).
(10) Bartlett, Hetherington, Kvalnes, and Tremearne: J. Am. Chem. Soc. **52**, 1374 (1930).

SOME EXPERIMENTS WITH WETTING AGENTS

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The surface activities of members of the homologous series of aliphatic acids and their sodium salts have been reported by various investigators (1). These substances show, in general, increasing surface activity, or ability to lower the surface tension of water, with increase in length of the carbon chain in agreement with Traube's rule. The measurement of the surface activities of some sulfonates of the benzene series was undertaken to show the influence of the nature of the substituent alkyl group and of its position in the benzene nucleus in relation to the polar sulfonate group.

Recently new types of compounds in which the active or polar part of the molecule is a sulfate or sulfonate group have been developed commercially and widely recommended as ideal detergents, wetting and penetrating agents The stability of solutions of these compounds in the presence of acids and in hard water permits their application under conditions which would prohibit the use of soap. The uses, advantages, and method of manufacture of one class of these products, the "sulfonated" higher alcohols, have been discussed by Killefer (2). Our experiments were extended to measure the adsorption or rate of exhaustion of such compounds from their water solutions by wool, and to study their effect when used as leveling agents in dyeing.

I. PREPARATION OF SULFONATES AND SURFACE TENSION MEASUREMENTS

The sulfonation of benzene, toluene, xylene, and cymene was accomplished by the general method of Gatterman (3), using fuming sulfuric acid and the minimum temperature required for each reaction. The sodium sulfonate was precipitated by treating the reaction products with saturated sodium chloride solution, or was obtained by neutralization with sodium hydroxide and evaporation. The sodium sulfonate was then purified by recrystallization from absolute alcohol or acetone until it was free of sulfate. Acetone was the more effective medium for the purification of the higher members of the series. Ethylbenzene, isopropylbenzene and butylbenzene were prepared by the Fittig synthesis (4), were then sulfonated, and their sodium salts obtained and purified as described above.

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Solutions of these salts in distilled water were prepared and their surface tensions were measured over a range of concentrations at a constant temperature of 18°C. These measurements were made by means of an improved torsion balance which was fully described by De Gray (5) in a recent article. The static or equilibrium surface tension values for these solutions are shown in figure 1.

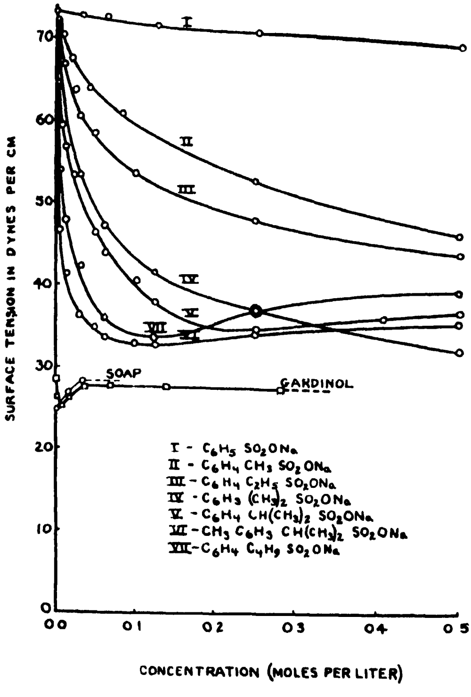

FIG. 1 LOWERING OF SURFACE TENSION BY SULFONATES OF BENZENE SERIES

In the case of sodium benzenesulfonate the observed lowering of the surface tension of water is roughly proportional to the concentration of the solute. In this its effect is similar to that of the lower members of the aliphatic series of acids or their salts and, in general, of substances in true solution which decrease surface tension. Beyond this first member the curves show increasing tendency to sag or to deviate from the straight-line relationship as the alkyl substituents increase in length or complexity. It is of interest to note that although the sulfonates of ethylbenzene (curve III) and xylene (curve IV) are identical in molecular weight, the latter is considerably more effective in lowering the surface tension of water.

This indicates that two substituent groups increase the surface activity of the compound more than a single group containing the same total number of carbon atoms. This point is exemplified further in the curves for the sulfonates of butylbenzene (curve VII) and cymene or *p*-methylisopropylbenzene (curve VII). These two curves also exhibit a minimum which is a characteristic of active surface-tension depressants and usually indicates a colloidal condition of the solute. With the exception of sodium benzenesulfonate, the solutes represented by the curves in figure 1 are probably mixtures of isomers.

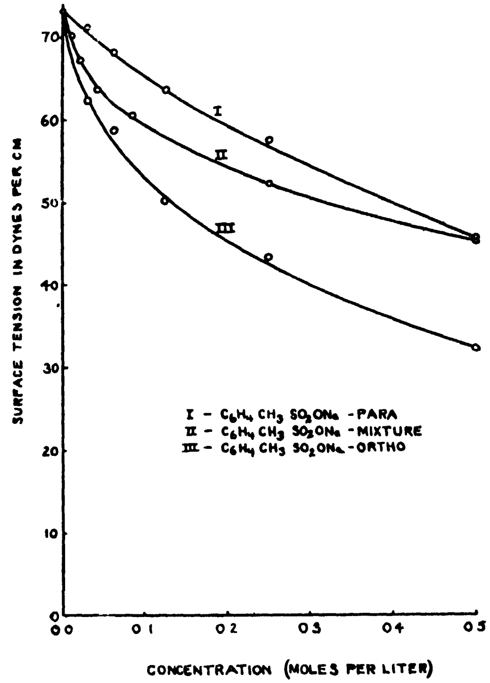

FIG. 2 COMPARISON OF *o*- AND *p*-TOLUENESULFONATES

In the sulfonation of toluene a mixture of two isomers is obtained. This mixture is composed of approximately 70 per cent of the para and 30 per cent of the ortho isomer. These two isomers were separated by taking advantage of the different melting points of the corresponding toluenesulfonyl chlorides, according to the method recommended by Beilstein (6). The *o*-toluenesulfonate and *p*-toluenesulfonate obtained from the separated sulfonyl chlorides were recrystallized from absolute alcohol, and surface tension measurements were made upon the solutions of each. These results are shown in figure 2 in relation to the curve for the mixture of the two isomers. It will be observed that the ortho derivative is more effective than the para as a surface tension depressant and that in low concentrations the activity of the ortho isomer predominates in the mixture, while in more concentrated solutions the surface activity of the mixture approaches that of the less active para component.

II. ADSORPTION OF WETTING AGENTS BY WOOL

For these experiments a fine grade of virgin wool was thoroughly degreased by scouring with soap and sodium carbonate, rinsed with distilled water and air dried. It was kept at constant humidity to attain a moisture content of approximately 13 per cent. Samples of wool weighing 5 g. were soaked for one hour at 50°C. in 500 cc. of the solutions of the wetting agents. The wetting agents used were the commercial products known as "Gardinol C.A." (compound A) and "Igepon T" (compound B). Both are sodium salts, the former a sulfate of a higher alcohol (2) and the latter a sulfonate of a condensation product. The solutions contained 0.5 per cent of the wetting agents and were made acid or alkaline by the addition of hydrochloric acid or sodium hydroxide. The pH values were determined colorimetrically at the end of the soak by means of standard indicators.

The percentage exhaustion of the wetting agent by adsorption was determined, after removing the wool, by evaporating 100-cc. portions of the solutions, drying the residue at 100°C. in an oven and weighing it. When hydrochloric acid or sodium hydroxide had been used to change the pH of the solution, this was carefully titrated and the weight of the salt formed was subtracted from the weight of the residue. This weight was also corrected for the weight of wool dissolved by the solution in each case. The actual proportion of wetting agent adsorbed by 5 g. of wool from 500 cc. of solution was obtained by comparing the corrected weight of the residue with the weight of residue resulting from 100 cc. of a solution of the wetting agent in which no wool had been soaked. The results, expressed as percentage exhaustion from solution, are represented in figure 3. Since the weight of wool used in each experiment was twice the weight of wetting agent present in the solution, the adsorption percentages based upon the weight of wool will be one-half the values represented by the curves in figure 3. For example, at pH 1.5 the solution of compound B is 22.9 per cent exhausted; under these conditions the wool has adsorbed 11.45 per cent by weight of this wetting agent. The experiments show that these substances are adsorbed from solution by wool in appreciable amounts only in acid solutions and that the amount of adsorption increases with increase in hydrogen-ion concentration.

These results can be interpreted by considering the nature of the compound in relation to the variation in the electrical charge of wool with change in pH. The wetting agents are sodium salts which, in water solution, produce surface-active anions containing a polar group and a long carbon chain. These negative ions are similar to the color ions of acid dyes and are similarly adsorbed by wool which bears a positive charge in acid solutions. The isoelectric point of wool, as reported by Harris (7), occurs at pH 3.4. Some adsorption of the wetting agent occurs beyond this point, just as the adsorption curves of acid and basic dyes overlap to some extent. However, as the acidity decreases beyond pH 3.4, the negative charge on the wool rapidly increases, and in this condition the wool repels the negatively charged ions so that no measurable adsorption occurs in this region. It is generally recognized that soap is not selectively adsorbed from its solution (pH 10–11) by textile fibers; the explanation of this fact is obvious, since the surface-active ion (or ionic micelle) of soap is likewise negatively charged.

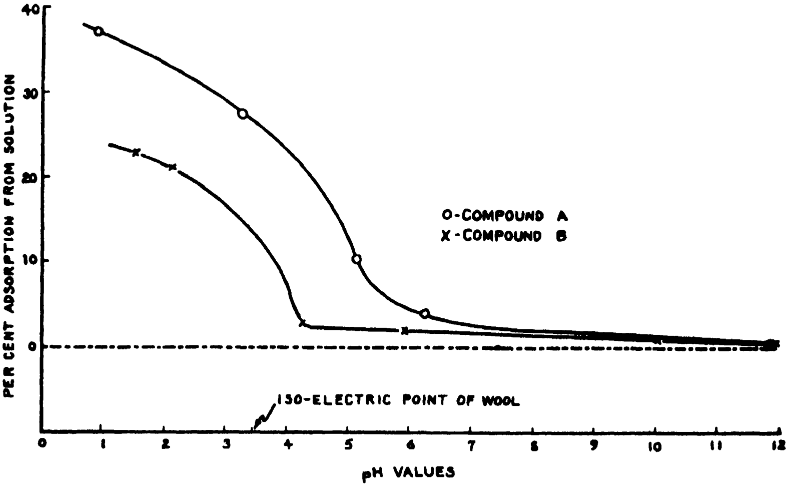

FIG. 3. THE ADSORPTION OF WETTING AGENTS BY WOOL

The practical conclusion to be drawn from these experiments is that, although they are stable in acid solutions, the new types of wetting agents are so strongly adsorbed from solutions of high acidity that they can hardly be employed economically under these conditions.

While no compounds furnishing positive ions of high surface activity were available for testing, it may be predicted that such substances would, like basic dyes, be strongly adsorbed by wool from alkaline solutions and negligibly adsorbed from acid solutions.

III. THE INFLUENCE OF WETTING AGENTS UPON THE ADSORPTION OF ACID AND BASIC DYES BY WOOL

The wool used for these experiments was a fine, white worsted knitting yarn. It was maintained at constant humidity, and one meter (about 0.5 g.) was accurately weighed for each test. Methylene blue was used as the basic dye at a concentration of 0.2 per cent, the acid dye was Orange II, and the concentration of the dye solution was 0.1 per cent in this case. Series of experiments with each dye were also performed in which Gardinol was added to the extent of 0.1 per cent and 0.5 per cent of the weight of the solution. The samples of wool were boiled for 2 minutes in 50-cc. portions of the dye solutions, which were made acid or alkaline with sulfuric acid or sodium carbonate respectively. Each sample of wool was transferred from the dye bath to distilled water and boiled for 2 minutes. It was then placed in an Erlenmeyer flask, covered with distilled water, and the air was displaced by carbon dioxide. The contents of the flask were heated to boiling and the dye on the wool was titrated with titanous chloride, using a slight excess of this reagent. The boiling was continued until the color was completely discharged and the excess of titanous chloride was then titrated with a solution of the same dye which served as its own indicator. A steady stream of carbon dioxide was passed through the flask throughout the titration. The pH values of the dye baths were obtained, after removing the wool, by means of a quinhydrone electrode.

The results for the acid dye are shown in figure 4 and for the basic dye in figure 5. The percentages are based upon the weight of the wool. Quantitative data for the adsorption of acid and basic dyes have been published by Briggs and Bull (8), who also studied the effect of the addition of salts to the dye bath. The results represented by curve I for each dye are consistent with the data of Briggs and Bull and with Bancroft's generalizations for the adsorption of dyes (9). With regard to the influence of the wetting agent or leveler, this can again be interpreted from a consideration of the nature of the surface-active ion in relation to the electrical condition of the wool. As shown in figure 3, Gardinol is strongly adsorbed by wool in acid solutions and, since its active ion is negative, this interferes with and decreases the adsorption of an acid dye in which the surface-active ion is also negative. In the case of the basic dye in which the active ion is positive, its adsorption is increased in acid solutions by Gardinol because of the strong adsorption of the negative ion of Gardinol. This is entirely consistent with Bancroft's statement that a readily adsorbed anion will increase the adsorption of a basic dye and decrease the adsorption of an acid dye. However, in alkaline solutions the adsorption of the basic dye is decreased by the Gardinol. This is apparently in contradiction to the rule just stated, but is not so in reality since, of course, an anion is not "readily adsorbed" by wool in an alkaline solution. The ability of Gardinol to decrease the adsorption of the basic

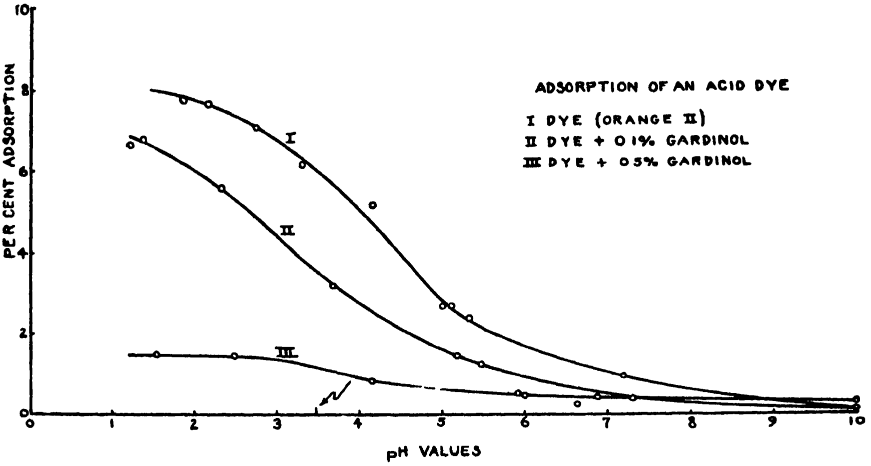

FIG 4 THE INFLUENCE OF A LEVELING AGENT UPON THE ADSORPTION OF AN ACID DYE BY WOOL

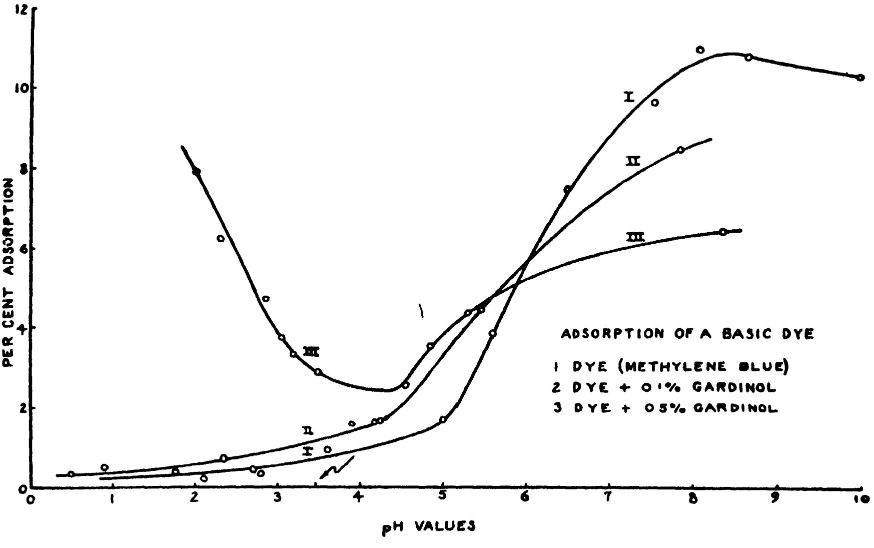

FIG. 5. THE INFLUENCE OF A LEVELING AGENT UPON THE ADSORPTION OF A BASIC DYE BY WOOL

dye in alkaline solutions may be attributed to its peptizing or detergent action, or its negative ion (or micelle) may be thought of as competing with the negatively charged wool for the dye cation.

SUMMARY

1. A number of the sulfonates of the benzene series have been prepared and the effect of the nature and position of substituent groups upon their surface activities has been studied. The surface tension–concentration relations of these products are compared with those of soap and other wetting agents.

2. The adsorption of some commercial wetting agents by wool has been measured in solutions having various hydrogen-ion concentrations. It is shown that, for substances of this type, the adsorption parallels the potential curve of the wool in acid solutions and is negligible in alkaline solutions.

3. The influence of wetting agents upon the take-up of acid and basic dyes by wool at various hydrogen-ion concentrations has been determined quantitatively. These agents increase the take-up of basic dyes in acid solutions and decrease dyeing under other conditions. The results are interpreted in terms of the electrical condition of the fiber and the adsorption of the surface-active ions.

REFERENCES

(1) Freundlich: Colloid and Capillary Chemistry, pp. 61–71. E. P. Dutton and Co., New York (1926).
(2) Killefer: Ind. Eng. Chem. **25**, 138 (1933).
(3) Gatterman: Practical Methods of Organic Chemistry, p 280. Macmillan and Co., New York (1915).
(4) Reference 3, p. 276.
(5) De Gray: Ind. Eng. Chem., Anal. Ed. **5**, 70 (1933)
(6) Beilstein: Handbuch der organischen Chemie, 4th Ed., Vol. XI, p 83.
(7) Harris: Bur. Standards J. Research **8**, 779 (1932). Research paper No. 451.
(8) Briggs and Bull: J. Phys Chem **26**, 845 (1922).
(9) Bancroft: Applied Colloid Chemistry, pp. 133–6 McGraw-Hill Book Co., New York (1926).

THE MECHANISM OF THE FORMATION OF KOHLSCHÜTTER'S SILVER SOL

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The colloidal dispersion commonly referred to as Kohlschütter's silver sol (1) is prepared by conducting a stream of hydrogen into a solution of silver oxide containing an excess of the solid oxide and maintained at a temperature of 50–60°C. Kohlschütter believed that the reduction took place on the walls of the vessel, both because the color of the sol varied with the nature of the vessel, and because in glass vessels of a given kind the velocity of the reduction was apparently directly proportional to the surface of the vessel exposed to the solution and inversely proportional to the volume of the solution. Thus in Thüringen soft glass and in quartz the sols were usually yellow-brown in color, and in Jena glass they varied from red through reddish-brown to violet and blue. In every case sol formation was accompanied by the deposition of a heavy black "mirror" of metallic silver on the vessel walls. The solubility of the glass was not regarded as an important factor in determining the nature of the sol, since the color of a sol formed in a certain kind of glass was the same even though the silver oxide solution used had been previously allowed to stand for a considerable time at 60°C. in another kind of glass.

Kohlschütter found that relatively large amounts of unreduced silver oxide remained in a sol even after prolonged treatment with hydrogen. The excess oxide may be removed by passing hydrogen through the sol contained in a platinized platinum vessel protected from the air with a bell jar. By this procedure the excess oxide was reduced, the silver depositing on the platinum vessel. The conductivity of the sols was reduced to 4 to 8 $\times 10^{-6}$ mhos, which was approximately one-tenth that of the original sols without any appreciable change in their appearance. On analysis he found, however, that the amount of silver in the colloidal particles had decreased during the purification process, and from this he deduced that the colloidal particles in the original sol contained some oxide. Since in general the particles in the yellow-brown sols contained more oxide than the particles in the reddish to blue sols, Kohlschütter claimed that the walls of the containing vessel determine the ratio of silver to silver oxide in a sol, as well as its color.

Erlach and Pauli (2) observed that a sol prepared by Kohlschütter's method, using hydrogen from a Kipp generator, always contained sulfur which came from hydrogen sulfide present in the hydrogen. Starting with pure silver oxide and pure electrolytic hydrogen there was said to be no sol formation in a hard glass or a silver vessel, but if a trace of potassium carbonate, sodium hydroxide, or ammonium hydroxide was added to the silver oxide solution a stable sol resulted. As a matter of fact, sols were obtained with electrolytic hydrogen, formed by electrolysis of sodium hydroxide, unless the gas was washed with concentrated sulfuric acid which was supposed to take out "alkali mist." The effect of alkali was attributed to the formation of an argentate, such as NaAgO, which served as the stabilizing electrolyte for the sol. In support of this they confirmed Kohlschütter's observations that the colloidal particles contained up to 20 per cent of unreduced silver. The stabilizing effect of a trace of hydrogen sulfide was attributed to the formation of some silver complex, but it is not obvious what this would be or how it would form.

Pauli's explanation of the necessity for sol formation of having either alkali or hydrogen sulfide in the reduction mixture is open to question. Pauli was unable to prepare a sol with pure silver oxide and pure hydrogen, but he was also unable to prepare a stable sol by the Bredig method in pure water. Best and Cox (3) had no difficulty with the latter preparation when they hit upon the right conditions and it seemed probable that a sol would result with pure hydrogen and silver oxide if one knew how to do it. As a matter of fact, the experiments to follow will disclose that silver sol formation by Kohlschütter's method is not determined either by the catalytic effect of the walls of the containing vessel, as stated by Kohlschütter, or by the presence of a substance capable of forming a complex negative stabilizing ion, as assumed by Erlach and Pauli.

EXPERIMENTAL

Procedure and reagents

The experimental procedure consisted simply in conducting hydrogen into silver oxide solutions in different kinds of glass vessels at a temperature ranging from 50–60°C. and noting what took place. Special attention was taken in the preparation and handling of the reagents. The silver oxide was precipitated from $N/10$ silver nitrate with a slight excess of $N/10$ sodium hydroxide, and washed ten times by decantation with boiling distilled water. A saturated solution was prepared by continuous shaking of a large excess of the solid oxide with 250 cc. of water for three to four hours. The entire process was carried out in the dark and the solutions were stored in the dark. Conductivity water from block tin stills was used throughout. The hydrogen was prepared by the process of Cooke and Richards (4).

The generator which contains the system, zinc amalgam–dilute hydrochloric acid–platinum, has been found to give hydrogen whose only impurity is a small amount of gaseous hydrogen chloride. To remove the latter the gas was passed over solid potassium hydroxide, then washed through distilled water and, as a final check on its purity, it was passed through a wash-bottle containing silver oxide solution before being conducted into the silver oxide solution in the reduction vessel.

The reduction vessels were test tubes with a hydrogen inlet tube of the same material. This type of vessel was chosen since it required the use of less of the pure reagents and assured thorough mixing and more intimate contact between the reacting compounds and the vessel walls. All connections in the gas train were glass to glass with one exception. Since a quartz reduction vessel and inlet tube was employed in some cases, the end of the quartz inlet tube was held against the end of the glass tube from the wash train by a short piece of gum rubber tubing which had previously been cleaned in a boiling sodium hydroxide solution and soaked in melted paraffin in a vacuum so that as the pressure was released into the evacuated space, the pores of the rubber were filled with the paraffin. This treatment of rubber has been found quite satisfactory in microanalytical work to prevent the rubber from giving off organic vapors and hydrogen sulfide. The same method of connection was used for all types of inlet tubes, for the sake of uniformity of procedure.

The reduction mixture was kept at the desired temperature by immersing in a water bath consisting of a 1-liter beaker of water heated by the flame from a microburner. The temperature was readily maintained within the desired limits and observations were easily made. A few drops of paraffin oil on the surface of the water decreased evaporation and this facilitated the maintenance of a constant temperature for long intervals.

Between runs the reduction vessels and the hydrogen inlet tubes were thoroughly cleaned as follows: The vessels were (1) soaked in concentrated nitric acid for six to twelve hours, (2) boiled with concentrated nitric acid for 5 minutes, (3) washed with distilled water and soaked for twelve to fifteen hours in several changes of distilled water, and (4) steamed for 5 minutes just before using.

Reduction of saturated silver oxide in the presence of excess solid

In order to test the effect of the containing vessel on the nature of the sol, mirror formation, and the action on solid silver oxide, observations were made with vessels of soft glass, Pyrex, and quartz. The results are summarized in table 1.

At the end of each of the above experiments the excess solid silver oxide was collected and, after washing several times with distilled water, it was found to be only partially soluble in dilute nitric acid (0.01 *N*) and in aqueous ammonia. The residues were washed and found to dissolve in concentrated nitric acid. From this it is apparent that the solid particles were partially reduced to metallic silver, the process being retarded gradually as the surface became coated with a silver film. Kohlschütter's statement that the solid silver oxide was not acted upon is obviously not in accord with the facts.

Although the differences in the colors of the sols were quite apparent, they were not as marked as would have been expected from Kohlschütter's report.

TABLE 1

Reduction of saturated silver oxide solution containing an excess of solid silver oxide

Temperature 55–58°C.

REDUCTION VESSEL	OBSERVATIONS		
	After a few minutes	After 3 to 4 hours	After 12 hours
Soft glass	Weak sol; silver mirror on walls.	Sol light yellow-brown in (T)* and yellow in (R)† Deposit on wall increasing.	Dense sol, deep yellow-brown in (T) and dark gray to brown-green in (R) Heavy black mirror on walls of inlet tube and containing vessel.
Pyrex	Weak sol; silver mirror on walls	Sol light yellow-brown in (T) and grayish yellow-green in (R) Deposit on walls increasing	Dense sol, deep brown with a reddish tinge in (T) and grayish yellow-green in (R). Heavy black mirror on walls
Quartz	Weak sol; no mirror	Sol yellow-brown in (T) and yellow-green in (R); no mirror.	Dense sol, deep yellow-brown in (T) and dark brownish-green in (R); no mirror.

* (T) = transmitted light
† (R) = reflected light

Reduction of silver oxide solution in the absence of excess solid

Since solid silver oxide is reduced by hydrogen at 55–60°C., observations were made of the effect on the sol formation process of eliminating the excess suspended solid. The results are given in table 2.

The above sols attained their maximum color after three to four hours, showing no perceptible darkening thereafter. The black mirror deposit likewise deepened very little after the first few hours. In every case the sols contained appreciable amounts of silver in solution even after prolonged treatment with hydrogen.

Reduction of ultrafiltered solutions of silver oxide

Since reduction of filtered silver oxide solutions with hydrogen gave only weak yellow sols in spite of the fact that they contained considerable unreduced silver in solution, it seemed probable that the substance reduced was not the silver in solution but colloidally dispersed silver oxide that was not removed by filtration through an ordinary filter. In support of this it was found that the saturated solutions, such as used in the preceding experiments, always contained appreciable amounts of colloidally dispersed oxide. To remove this in so far as possible, the saturated solution was ultrafiltered before use. For this purpose a filtering membrane was prepared by impregnating No. 40 Whatman filter paper with collodion from a 4 per cent solution in glacial acetic acid. The membrane was used in a gold-plated ultrafilter in which the wire gauze usually employed was replaced with a sheet of perforated gold foil. At a pressure of 40 lbs. per square inch, 125 cc. of solution was filtered in 5 minutes. Filtration with a cellophane membrane was unsatisfactory, since it reduced the silver solution completely. The observations with ultrafiltered solutions in various vessels are given in table 3.

TABLE 2

Reduction of filtered saturated silver oxide solution

Temperature 55–58°C.

REDUCTION VESSEL	OBSERVATIONS		
	After 1 hour	After 5 to 6 hours	After 12 hours
Soft glass	Very weak sol; thin silver mirror on walls	Light yellow sol; some darkening of mirror.	Almost the same as after 5 to 6 hours
Pyrex	Very weak sol; thin silver mirror.	Light yellow sol; some darkening of mirror.	Almost the same as after 5 to 6 hours
Quartz	Extremely weak sol; no mirror.	Light yellow-brown sol; no mirror.	Almost the same as after 5 to 6 hours

TABLE 3

Reduction of ultrafiltered solutions of silver oxide

REDUCTION VESSEL	OBSERVATIONS
Soft glass	Silver mirror starts to form after 1 hour and darkens gradually; little or no sol formation in 35 hours; silver ion in the solution.
Pyrex	Silver mirror starts to form after 1 to 2 hours and darkens slowly; no sol formation in 35 hours; silver ion in the solution.
Quartz	No sol formation and no mirror formation even after 100 hours; nephelometric analysis shows no loss in silver ion concentration.
Platinum (quartz + platinum foil)	No sol formation; no deposit on quartz tube; after 12 hours all the silver deposited on the platinum foil in the form of minute hexagonal platelets.
Silver (quartz + silver foil)	No sol formation or deposition of silver on either the walls of the quartz vessel or the silver foil.

The results shown in table 3 furnish conclusive evidence that silver oxide in true solution is not reduced in a quartz or silver vessel by hydrogen. Since there is no action in a quartz container, silver or platinum foil in a quartz vessel is equivalent to a container of the metal in question.

The reduction of dissolved silver oxide in the presence of platinum is due to catalytic activation of the hydrogen at the surface of the metal. As a result, hydrogen goes into solution as hydrogen ion and an equivalent amount of silver ion leaves the solution, giving a minute nuclear deposit of silver at certain points on the platinum surface. As the process continues, these nuclear deposits grow to relatively large hexagonal platelets of silver. This phenomenon does not take place at a silver surface because hydrogen is not catalytically activated to any appreciable extent by silver, under the conditions of the experiment.

The ease with which solid silver oxide, in suspension or on the walls of the vessel, is reduced by hydrogen indicates that hydrogen is activated at the surface of silver oxide or at the interface silver–silver oxide (5).

The reduction at the surface of the glass vessels with the formation of a mirror-like deposit is probably preceded by the formation of a film of silver oxide, which is subsequently reduced. The deposition of a silver oxide film is due either to adsorption from solution or to precipitation by means of alkali dissolved from the glass. In support of the latter view it has been found by H. L. Johnston[1] at Ohio State University, that the solubility of silver oxide in water, 2.2×10^{4} equivalents per liter,[2] is reduced enormously by the presence of very small amounts of alkali. Thus 0.02 *N* alkali reduces the solubility to 6×10^{6} equivalents per liter, which is approximately 3 per cent of the solubility in pure water. At a temperature of 50–60°C. sufficient alkali is extracted from the glass to cause the deposition of a film of oxide which is promptly reduced. Continuation of the process causes a gradual thickening of the mirror thus deposited. The process is in no sense a result of the catalytic activation of hydrogen by the glass surface. No film formation occurs on a quartz vessel because of the insolubility and non-alkaline character of the surface.

Further evidence in support of the above conclusions is furnished by the results of three experiments in which very dilute alkali, colloidal silver oxide and colloidal silver, respectively, are added to the ultrafiltered solution in a quartz vessel before conducting in the hydrogen. The silver oxide sol was formed by saturating and filtering a solution at 100°C. and cooling. The results are given in table 4. These observations support the view that sol formation and mirror formation by Kohlschütter's method result from reduction of solid silver oxide and not of the dissolved compound. Colloidal silver, like silver in mass, does not catalytically activate the hydrogen and effect reduction.

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[1] Private communications.

[2] Kohlschütter believed the solubility of silver oxide to be twice this value. The most probable explanation is that Noyes and Kohr (J. Am. Chem. Soc. **24,** 1143 (1902)) reported a value of 2 16 $\times 10^{-4}$ moles per liter, but their data shows that they meant to say 2 16 $\times 10^{-4}$ equivalents per liter.

Because of the precipitation of silver oxide by the alkali extracted from glass, an ultrafiltered solution stored in a Pyrex flask for two weeks gave a light yellow sol on reduction in a quartz vessel. The precaution was therefore taken to store the stock solutions in quartz. The very slow formation of a weak sol in a glass vessel with the ultrafiltered solution may result from the breaking-off of pieces of the mirror first deposited on the walls, or of silver oxide itself before the latter is reduced.

TABLE 4

Reduction in a quartz vessel of ultrafiltered silver oxide solutions after certain additions

ADDITIONS	OBSERVATIONS
Solution made 2 to 5 × 10^{-4} to sodium hydroxide	Weak sol after 1 hour; light yellow to yellow-brown sol after 4 to 5 hours; no mirror; colorimetric examination shows that the depth of color increases with the sodium hydroxide concentration but not in direct proportion.
Colloidal silver oxide	Sols are formed, the depth of color of which was found by colorimetric analysis to be directly proportional to the amount of colloidal silver oxide added; no mirror formation.
Colloidal silver	No reduction of the solution and no mirror formation even after 30 to 40 hours.

Reduction of silver oxide solutions formed by diluting the saturated solution

In the experiments considered in the last section there is one possible source of error. In the ultrafiltration process to remove all silver oxide nuclei, the solution came in contact with both the ultrafiltration membrane and the rubber gasket. The possibility that some foreign substance was introduced which would inhibit the reduction process was not excluded. To get around this possible source of error, the colloidal silver oxide was removed from the saturated solution by diluting with enough water to dissolve the colloidal oxide. The dilutions were made in quartz vessels and the resulting solutions were allowed to stand for three to four days to establish equilibrium conditions. Some observations with such solutions are given in table 5.

It is apparent from the above experiments that a filtered saturated solution diluted in the ratio of 6 of solution to 4 of water is not reduced at all by hydrogen in a quartz vessel at 50–60°C. The solution diluted in the ratio of 7:3 showed barely perceptible sol formation. The obvious explanation is that the dilution in the ratio of 6:4 is sufficient to remove all colloidal oxide, thus eliminating reduction with the formation of silver sol. In soft glass at this dilution, mirror formation proceeds slowly and sol formation is extremely slow. The common ion effect of the alkali from the glass is localized at the surface, depositing a film of oxide which is subsequently reduced. If the dilution is in the ratio of 1:5, the alkali from the glass is insufficient to precipitate the oxide and no mirror formation results. This indicates that the precipitating action of alkali is a more important factor in the formation of a film of silver oxide on the glass than adsorption of silver oxide from solution by the glass wall. For if the latter were the important thing, one would expect some mirror formation from the diluted solution, especially since the adsorption is in general proportionately greater from more dilute solutions. The absence of mirror formation in quartz and silver with saturated solutions likewise indicates that the precipitating action of alkali from glass is more important than adsorption of silver oxide from solution, as the initial step in mirror formation.

TABLE 5

Reduction of silver oxide solutions formed by reducing saturated solutions

REDUCTION VESSEL	DILUTION Solution water	OBSERVATIONS
Quartz	5:5	No sol and no mirror even after 30 to 40 hours.
Quartz	7:3	Very light yellow sol in 10 to 12 hours; no mirror.
Quartz	6:4	No sol and no mirror even after 30 to 40 hours.
Soft glass	6:4	Faint mirror after 2 hours, darkening gradually; very light yellow sol in 30 hours.
Soft glass	1:5	No sol and no mirror even after 30 hours

Samples of solutions diluted in the ratio of 6:4, which are not reduced at all in quartz, were treated with alkali, colloidal silver oxide, and colloidal silver in the same way as the ultrafiltered solutions considered in the last section. The results were identical with those recorded in table 5 and are therefore not repeated here. These observations merely confirm the observations with ultrafiltered solutions and show that no complication was introduced by the ultrafiltration process.

In this connection it may be mentioned that the solubility of silver oxide determined by chemical methods is approximately 2.2×10^{-4}, while that by conductivity methods is 1.38×10^{-4} equivalents per liter (6). From this it is assumed that the silver hydroxide which is formed in solution is approximately 60 per cent dissociated. In view of the fact that 4 parts of water must be added to 6 parts of saturated silver oxide as ordinarily prepared in order to get rid of all colloidal silver oxide, it is suggested that the higher values of the solubility as determined by chemical methods may be due in part to the presence of some colloidally dispersed oxide in the solution. This question is now being investigated.

Effect of purity of the hydrogen on sol formation

It will be recalled that Pauli and Erlach failed to obtain silver sols in Pyrex vessels with pure solutions and electrolytic hydrogen freed from "alkali mist" with sulfuric acid. Since we always obtained sols with hydrogen, free from alkali, provided the saturated solution was not ultrafiltered or diluted to eliminate colloidal silver oxide, the failure of Pauli and Erlach to obtain sols must be explained on some basis other than purity of hydrogen. There are two possibilities: either the silver oxide solutions which they used were too dilute to give sols or mirrors with glass (see table 5), or the sulfuric acid used in the washing train to remove alkali mist substituted a sulfuric acid mist in its place. Since they doubtless worked with saturated solutions, the latter explanation appears the more probable. At any rate it was shown that a filtered saturated silver oxide solution which contained colloidal silver oxide gave no mirror or sol on treating with hydrogen for forty hours provided the solution was made 10^{-3} N with sulfuric acid. With 10^{-4} N acid very slight sol and mirror formation was observed after twelve hours. Sulfuric acid added directly or with the hydrogen has the same effect as dilution in removing silver oxide particles and in preventing the deposition of a silver oxide film on the walls of the vessel.

The results of this investigation may be summarized briefly as follows:

1. The formation of Kohlschütter's silver sol by the reduction of silver oxide with hydrogen at 50–60°C. is accomplished only in the presence of solid silver oxide. Saturated solutions that have not been ultrafiltered ordinarily contain appreciable amounts of the colloidally dispersed oxide.

2. In a quartz or silver vessel an ultrafiltered silver oxide solution undergoes no reduction with pure hydrogen at 50–60°C.; in a glass vessel the reduction is confined to the surface of the glass giving a thin mirror of metal: in a platinum vessel the reduction is at the surface of the metal, depositing relatively large hexagonal platelets of silver.

3. The reduction of silver oxide solution in a platinum vessel results from catalytic activation of the hydrogen at the platinum surface. There is no catalytic activation of hydrogen and no reduction at the surface of quartz or silver.

4. Mirror formation by reduction in glass vessels is not due to catalytic activation of hydrogen at the surface of glass as implied by Kohlschütter. The mirror formation is preceded by the deposition of a film of oxide which is subsequently reduced. The oxide film results chiefly from precipitation by means of alkali dissolved from the glass, but may be due in part to adsorption of the oxide from solution.

5. The ease with which solid silver oxide, in suspension or on the walls of the vessel, is reduced by hydrogen, indicates that hydrogen is readily activated at the surface of silver oxide or at the interface silver–silver oxide.

6. Pauli's view that sol formation will not take place except in the presence of alkali or sulfide which can furnish a complex stabilizing electrolyte, is not in accord with the experimental evidence herein recorded.

REFERENCES

(1) Kohlschütter: Z. Elektrochem. **14,** 49 (1908).
(2) Erlach and Pauli: Kolloid-Z. **34,** 213 (1924).
(3) Best and Cox: J. Chem. Soc. **1929,** 2727.
(4) Cooke and Richards: Am. Chem. J. **10,** 102 (1888).
(5) Cf. Pease and Taylor: J. Am. Chem. Soc. **43,** 2179 (1921).
(6) Böttger: Z. physik. Chem. **46,** 602 (1903).

NOTE ON THE POSSIBLE MAGNITUDE OF THE SORPTION ERROR IN MEASUREMENTS INVOLVING EASILY SORBABLE GASES AT LOW PRESSURES

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INTRODUCTION

Gases which are easily compressible condense readily as a rule on surfaces exposed to them. At sufficiently high pressures changes in the amount of gas condensed on the walls of an apparatus, resulting from alterations in the pressure, are small compared with changes in the quantity of gas contained in the free space of the apparatus. They may therefore be neglected, except in cases where a high degree of accuracy is required; for example, in measurements of gaseous densities for atomic weight determinations. Not so, however, at low pressures. Here, not only the amount of gas contained in the free space of the apparatus, but also the amount sorbed on the enclosing walls may vary directly with pressure—the so-called "Henry range." If the initial slope of the sorption isotherm is greater than that of the isochor for the apparatus concerned the two curves will intersect, for the latter continues to rise, whilst the former tails off more or less rapidly as saturation of the surface is approached. In such cases calculations based on the pressure changes observed in an apparatus of known volume may be subject to serious error, and this may escape unnoticed unless there is some possibility of controlling the results by an independent method.

The diagram of figure 1 represents a case in which the free gas content at 20°C. of an apparatus of two-liter capacity is compared with the early portion of a typical sorption[1] isotherm at the same temperature. In general there is no necessity for the two curves to intersect, as in the hypothetical case depicted here. There will, however, usually be found a range of low pressure over which the slopes will not be widely different, and over this range the same remark applies.

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[1] In the absence of suitable data for glass the start of the 20°C. isotherm for sulfur dioxide on 0.05 g. of wood charcoal (writer's unpublished results) has been plotted. The smoothed curve is the commencement of a "Freundlich" equation, $A = 50.0 p^{0.787}$, where A is given in micromoles and p in millimeters of mercury. An equation of the Langmuir type, $A = \frac{124\,p}{1+5.52\,p}$, would fit the upper points of the figure reasonably well, but falls however below the first three points.

APPARATUS

The apparatus in which the experiments about to be described were performed, was constructed for the purpose of examining the suitability of the McLeod gauge as an instrument for measuring low pressures of sulfur dioxide. In that section of the apparatus with which we are here concerned (figure 2), the following combinations were independently possible:—

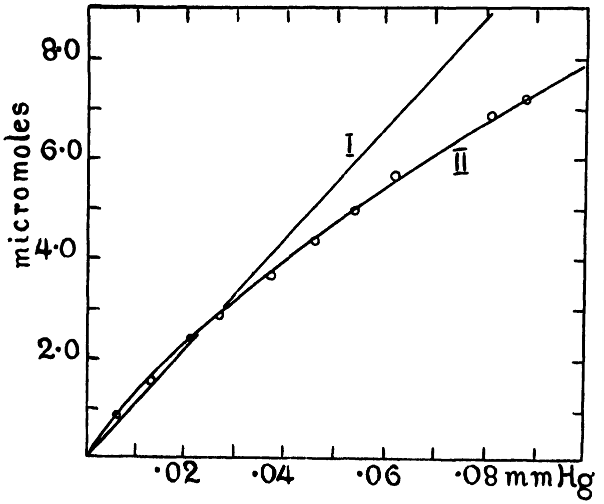
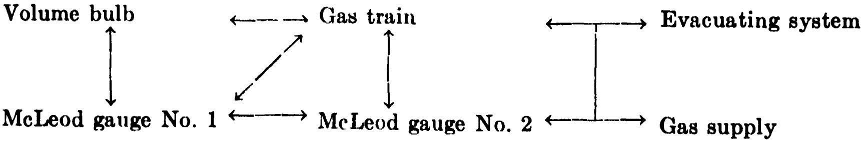


FIG. 1. *Curve I:* Isochor for apparatus of two-liter capacity at 20°C. May be considered a straight line for all gases over the pressure range here in question.

Curve II: Typical isotherm for easily condensible gas. Approaches a limiting saturation value at higher pressures unless capillary condensation intervenes.



The estimated surfaces and volumes of the different parts of the system bounded by taps or seals were as follows: gas train (T_1 to T_7), 750 sq. cm., 164 cc.; volume of bulb, R, 560 sq. cm., 997 cc.; McLeod gauge No. 1, G_1, 660 sq. cm., 319 cc.; McLeod gauge No. 2, G_2, 290 sq. cm., 269 cc. Volume estimates are probably more accurate than those of surface. The exact significance of estimates of the geometrical surface is uncertain, since calculations of sorption data based on such estimates in the case of glass indicate the existence of an unduly large number[2] of superposed layers of closely packed molecules under certain conditions

The two McLeod gauges were similar in size and shape, each having a bulb of ca 180 cc volume and a compression chamber consisting of a length of quill tubing of cross section equivalent to 7 29 cu mm per millimeter, surmounted by a capillary of 1 88 cu mm per millimeter At the highest mark a column of 1 cm of mercury corresponded to a gas pressure of 1 5 microns of mercury in the system The upper limit of the reading range of McLeod gauges was a pressure of 4 mm of mercury

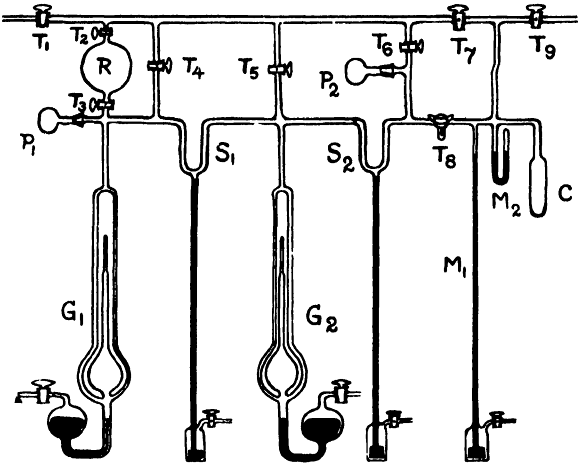


Fig 2 Apparatus Used in the Experiments

R, volume bulb, G_1 and G_2, McLeod gauges, C, condensation bulb containing phosphorus pentoxide, P_1 and P_2, phosphorus pentoxide drying bulbs, M_1 and M_2, manometers for controlling pressure of gas to be admitted to micropipette, T_8, single-bore, three-way tap with appendix forming micropipette, T_1, tap to evacuating system, T_9, tap to reserve of sulfur dioxide

Right-hand side of system —McLeod G_2, bounded by mercury seals S_1 and S_2 and by tap T_6 Left-hand side of system —McLeod G_1, bounded by S_1, T_3 and T_4, plus volume bulb R, plus gas train between T_1 and T_7

The two gauges were connected directly by way of a mercury seal, S_1, but for the remaining connections carefully chosen glass taps lubricated with rubber grease (later replaced by Apiezon) were employed Separating the system from the gas supply there was a capillary tap, T_8, with three outlets at 120° to one another but only one bore One of the outlets had been sealed off to form a short appendix, and by connecting this with the source of supply and the system successively, the pressure in the latter could be increased by amounts as small as desired, the pressure of the supply having been suitably adjusted beforehand. This tap, the only one bounding the system to have on the other side sulfur dioxide at appreciable pressures, could be isolated by a second mercury seal, S_2, introduced between it and the McLeod gauge G_2.

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[2] For example, circa fifty layers of water, five layers of carbon dioxide (Langmuir J Am Chem Soc **38,** 2283 (1916))

TREATMENT OF APPARATUS

Following the usual practice, the constituent parts of the apparatus had been cleaned with chromic–sulfuric acid[3] mixture before assembly. After completion of the air calibration, for which one of the McLeod gauges served as reference volume, the apparatus was exhausted thoroughly and baked out at 250–300°C. with the mercury vapor pump running. Heating elements in the form of nichrome wire spirals wound on Pyrex quill and mounted parallel to the axes of sheet asbestos cylinders, reinforced where necessary by a backing of sheet "tin," were found very convenient for heating the gauges, which for this reason had been mounted on iron stands instead of the usual form of wooden support. In order to permit of their easy removal when not in use the heating ovens were hinged down one side. During the baking-out of the McLeod gauges the gas train and volume bulb were heated at intervals by the aid of the spirit flame. A cowl of asbestos sheet suitably arranged prevented the formation of a cold cap on the upper hemisphere of the volume bulb.

The outgassing treatment was repeated each time the gas in the apparatus was changed and whenever the accumulation of surface moisture was suspected, owing to the attainment of an apparently negative pressure on exhausting[4] or to a drop in the calculated pressures on passing from mark to mark on the McLeod gauge.

EXPERIMENTAL PROCEDURE

The experiment consisted in distributing a certain quantity of sulfur dioxide at low pressure between the different sections of the apparatus and measuring the pressure in each side independently. After each redistribution the apparent quantity of gas present in the apparatus was calculated from the known volumes of the different sections and the observed temperatures and pressures. The total quantity was then compared with an arbitrarily chosen initial reading for which the whole of the free gas had been collected in McLeod gauge No. 2, hereafter referred to as the right-hand side of the apparatus. When equality of pressure had been attained in both sides of the system, a further transfer of gas could be effected by applying a wad of cotton-wool soaked in liquid air to an appropriate section of the train for a short time and manipulating the taps accordingly. By proceeding in this manner it was possible to distribute the gas in either direction at will from a state of uniform pressure, or to collect practically the whole[5] of the free gas in either side of the system.

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[3] This treatment, though customary in gas work, possesses the disadvantage of covering the surface of the glass with a layer of silica gel, thereby increasing the sorption characteristics of the apparatus (cf. H. S Frank: J. Phys. Chem. **33**, 970 (1929)). From this point of view swabbing out with cotton-wool soaked in benzene might be preferable, other things being equal, the solvent removing the grease and mechanical action the insoluble matter.

[4] Differences in the dryness of the surface of the glass in the compression chamber and its comparison capillary cause the depression of the mercury meniscus in the two to differ, although the diameters are the same in both (cf. L. Dunoyer: La Technique du Vide, p 74). The effect was frequently observed after unusually high temperatures had prevailed in the laboratory for some hours at a time. Under such conditions there is a disengagement of water from lower sorption levels, which the pentoxide bulbs in the train are not able to remove immediately.

RESULTS

The results of a typical series[6] of distributions in both directions, repeated three times, are given in figure 3, in which the percentage variation from the initial reading has been plotted against the time in days from the start. In order to avoid undue extension of the time scale the intervals between the last readings on one day and the first on the next have been omitted. Lines joining the experimental points merely indicate the sequence of the readings; they do not, in general, represent an attempt at intrapolation.

In the course of the first distribution from right to left an apparent disappearance of gas was observed, sorption on the new surface exposed more than counterbalancing desorption from the old consequent upon the pressure.drop in the right-hand side. Completion of the transfer was accompanied by a partial recovery of the loss. After returning the gas to the right-hand side of the system a gain of some 16 per cent (fifth day of figure 3) ensued, increasing to 20 per cent (eleventh day of figure 3) on repeating the cycle of operations. Sorbed gas was evidently being slowly disengaged from the enclosing walls of the system.

Since early experiments of Herbert[7] had already shown the impracticability of completely recovering sulfur dioxide sorbed on glass, even on raising the temperature, there did not appear to be any likelihood of success attending an effort at recovery from a system at room temperature. Accordingly no attempt was made to push the matter to a limit; instead, a condensation bulb in the system was immersed in liquid air for three periods of ten minutes or so and the whole of the condensed gas was then allowed to expand into (a) the whole, (b) the right-hand side, and (c) the left-hand side, respectively, of the system. The peaks on the thirteenth, fourteenth and fifteenth days of figure 3 represent the earliest points taken in each case.

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[5] There was always a small after-release of gas on isolating a section of the apparatus which had been exposed to liquid air for a short period of time; hence the transfer of gas never appeared to be quite complete on attempting to collect the whole of the free gas in one side of the apparatus.

[6] In all, three series of distributions were performed with different quantities of gas in the system in each case. For reasons of economy in space the intermediate series only is discussed here; the preceding and following series, with twice and half as much free gas, respectively, in the system yielded entirely analogous results.

[7] J. M B Herbert (unpublished work performed at Manchester University). F. P. Burt (Trans. Faraday Soc. **130**, 183 (1932)) reports that in the case of ammonia sorbed on glass several days exposure to the vacuum produced by charcoal cooled in liquid air is insufficient for the recovery of even half the quantity of gas sorbed during a week's run at atmospheric pressure.

It may be observed that the peak corresponding to the readings of the fourteenth day is double. This is due to the removal of a small quantity of permanent gas, which was found to have collected in the course of the experiments. It owed its origin in all probability to traces of air dissolved in the tap grease[8] during a check air calibration performed shortly before and now released under the combined influence of the low pressure in the apparatus and the high laboratory temperatures obtaining about this time on occasion. A correction based on the assumption of a uniform disengagement with time yields the dotted curve of figure 3; the general form of the curve is in no wise altered thereby and the effect is small compared with the other effects observed, so that a correction on this basis would appear to be not unjustified.

Examination of the curve of figure 3, particularly in the corrected form, indicates that, for all practical purposes, a state of quasi-equilibrium had been reached[9] at the beginning of the series of distributions, i.e., the purely time-conditioned effect was negligible. The increasingly large development of free gas on collecting in the right-hand side of the system would appear to be due to the hysteresis effect associated with the sorption of easily condensible gases on glass surfaces. Exposure of the system to the low sulfur dioxide pressure obtaining at liquid air temperatures effects the release from the glass of quantities of gas, which are not resorbed immediately on raising the pressure again.

The effect may be considered to be the counterpart of the phenomenon observed by Burt and Jones.[10] These observers found that in a sorbing system where sorption was proceeding with extreme slowness it was possible to cheat time, as it were, by temporarily raising the working pressure. On returning the system to the original pressure the sorption was found to

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[8] It is not practicable to heat the taps of an apparatus during the outgassing and thus accelerate the liberation of dissolved gases from the lubricant, consequently the last traces are released with extreme slowness.

[9] The apparatus had been standing at low pressure for a fortnight before the series was commenced

[10] F. P. Burt, loc. cit.

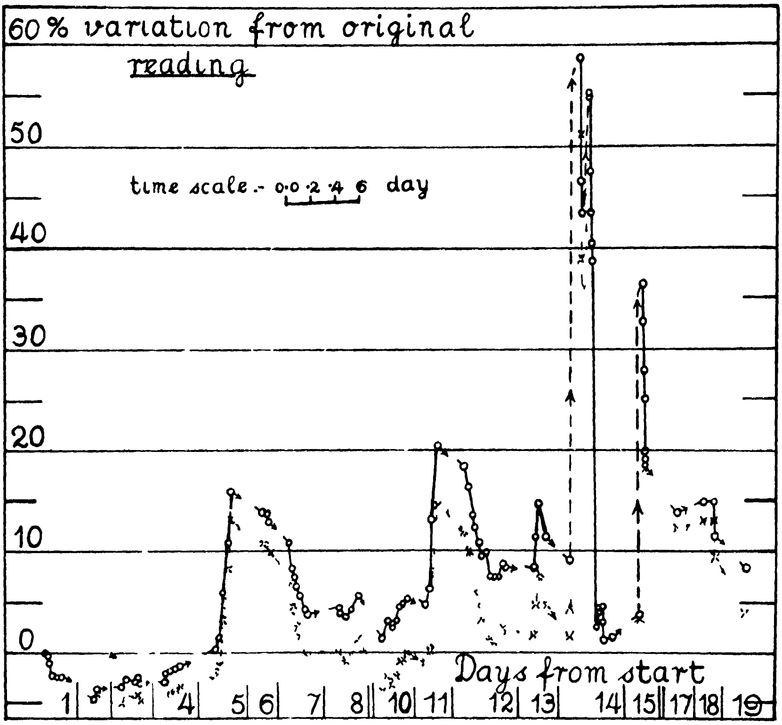

Fig 3 Variation of Apparent Free Gas in System Plotted Against Time from an Arbitrarily Chosen Starting Point

The lower, dotted line indicates that the truly time-conditioned desorption is practically nil; the main disengagement of gas is provoked by the low pressure resulting from the liquid air treatment

The pressures obtaining at the distributions corresponding to the salient points of the curve were as follows:

	Left-hand side	*Right-hand side*
Start‡	0 00004 mm. Hg	0 08318 mm. Hg
1st peak‡ (5th day)	0 00030 mm. Hg	0 09640 mm. Hg
2nd peak‡ (11th day)	0 00278 mm. Hg	0 08626 mm. Hg
3rd peak* (13th day)	0 01519 mm. Hg	0 01497 mm. Hg
4th peak‡ (14th day)	0 00098 mm. Hg	0 1311 mm. Hg
5th peak‡† (14th day)	0 00049 mm. Hg	0 1289 mm. Hg
6th peak§ (15th day)	0 02306 mm Hg	0 00010 mm. Hg

* After distributing throughout whole system.

† After removal of trace of permanent gas.

‡ Bulk of gas collected in right-hand side of system.

§ Bulk of gas collected in left-hand side of system.

have attained values which would not have been reached in reasonable time had the sorbing pressure been maintained constant throughout. In the present case we secure an increased desorption by temporarily reducing the pressure in the system to very low values.

The three peaks mentioned above (figure 3) are of interest for the light they throw on the loosely held surface gas in the system. Owing to the time required for the expanding gas to distribute itself throughout the different parts of the apparatus on evaporation some minutes elapse, after removal of the liquid air, before it is possible to take readings. Nevertheless, the three peaks are, qualitatively at least, in the relative positions we should expect to find in the case of a given quantity of sorbate admitted to (a) the whole, (b) the smaller part, and (c) the larger part, respectively, of a sorbing surface. Quantitative agreement is hardly to be expected in view of the difficulty of securing identical conditions in each case. If we suppose, however, that the relative positions of the peaks under consideration are, in the main, due to differences in the instantaneous sorption, it follows that the amount of gas actually condensed by the liquid air corresponds to a still greater departure from the initial reading than is indicated by the highest peak recorded in the figure, that of the fourteenth day.

CONCLUSIONS

From the foregoing it appears evident that, in an apparatus containing an easily sorbable gas at low pressures, there is, in addition to the free gas in the system as calculated from the known volumes and observed temperatures and pressures obtaining, an indeterminate amount of sorbed gas potentially available for release on reducing the pressure. This sorbed gas escapes observation under the usual conditions of experiment, though it may equal or even exceed in amount the free gas in the system. In the absence of time effects the gas would be difficult to detect, but by taking advantage of the time-lag in the attainment of sorption equilibria its presence may be revealed and an estimate, almost certainly too low, made of the amount involved.

In a typical apparatus containing sulfur dioxide a variation in the content of free gas amounting to more than 50 per cent referred to an arbitrary starting point, was observed. The ratio of surface to volume was not unduly large and the range of pressure variation in the system was from 0.0001 to 0.10 mm. of mercury, i.e., not excessively low.

Although the experiments described above were performed with sulfur dioxide in the system, the effect observed is in no way confined to this gas. It depends, as seen from figure 1, only on the relative shapes of the isochor and the sorption isotherm for the particular gas and apparatus concerned. Accordingly it may be expected to be present in any apparatus containing an easily sorbable gas at a sufficiently low pressure. Hence, in the absence of any control in the form of an independent method[11] of determining the quantities of substance involved, caution should be exercised in the interpretation of experimental results obtained under conditions similar to those considered above.

SUMMARY

1. Comparison of the forms of a typical sorption isotherm and the isochor of an apparatus of two-liter capacity indicate that, over a certain low pressure range, the gas sorbed on the walls of a relatively simple apparatus may approach or even exceed in amount that contained in the free space of the system.

2. In the absence of some independent form of control this sorbed gas may entirely escape detection, but by taking advantage of the time-lag in the attainment of equilibrium in the case of glass as sorbent we may nevertheless observe a part of the pressure-sensitive sorbed gas.

3. As an example, some measurements with sulfur dioxide are quoted, in the course of which a temporary disengagement of sorbed gas amounting to more than 50 per cent of the free gas at an arbitrary starting point was observed. The total quantity of sorbed gas in the system must have been still greater, since the instantaneous resorption could not be measured.

4. Attention is called to the necessity for exercising caution in the interpretation of experimental results involving measurements of pressure changes in apparatus containing easily sorbable gas at low pressures, viz., pressures below 0.1 mm. of mercury.

The experimental work on which this communication is based was performed at Frankfurt-am-Main during the tenure of a Fellowship awarded by the Alexander von Humboldt Stiftung, Berlin, to the Trustees of which the writer tenders his thanks.

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[11] Such an independent form of control might be furnished, in sorption work for instance, by the McBain sorption balance or some other suitable form of microbalance.

SOME OBSERVATIONS ON THE TRANSFORMATION OF CYCLOPENTADIENE INTO ITS DIMERIDE

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Cyclopentadiene is obtained in the first runnings of the crude benzene from coal tar, and readily polymerizes, at temperatures up to 100°C., yielding chiefly dimeride. Above this temperature polycyclopentadienes are also formed. The present experiments, which arose out of work in another connection, consisted essentially of an investigation of the rate of dimerization, utilizing for this purpose the accompanying fall in vapor pressure.

EXPERIMENTAL

The crude dimeride was distilled and the fraction collected which boiled at 172.5°C. This was then redistilled and kept in a stoppered bottle in the dark. Some of the pure dimeride was boiled with iron filings in a flask fitted with a fractionating column. Ice-cold water was run through the condenser and the distillate collected in a receiver surrounded with ice, the fraction being employed which passed over at 41°C. This monomeride changed over very rapidly into the dimeride and was therefore used immediately after it had been prepared.

The apparatus employed was extremely simple and is shown in figure 1. The container for the liquid, A, which was similar in design to that described by Chaplin (1), was attached to the apparatus by a waxed ground-glass joint B. A T-piece, C, made connection with the manometer, D, a long tube dipping into a mercury reservoir, which was open to the air, while the other arm of the T-piece connected through the tap E with a Kraus mercury condensation pump, backed by a Hyvac oil pump. Before each reading the zero was taken, and since the individual experiments only took a short time, there was no change in the zero over this period. This was checked by remeasuring after each pressure reading had been taken.

In order to avoid the adjustment of a thermostat to the rather troublesome temperature of 12°C., which had been fixed as suitable for the comparison of vapor pressures, which would fall, during the course of the experiment, from the high value given by the monomeride to the much lower figure of the dimeride, measurements were always made at a series of neighboring temperatures, the results being plotted in the form of log

$p:1/T$. The container was kept at room temperature between the readings, and that chosen (12°C.) represented the average room temperature during the year in which the experiments were made.

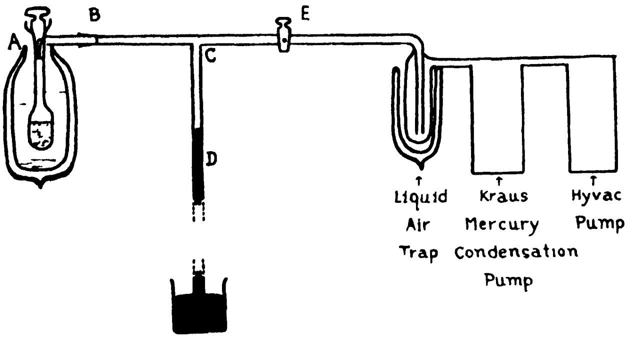

FIG. 1

TABLE 1

Zero reading = 27.98 cm.

TEMPERATURE	TIME AFTER OPENING CONTAINER	PRESSURE
degrees C	*minutes*	*cm* Hg
14.5	4	31 18
	7	31 22
	14	31 22
6.9	2	30 11
	6	30 25
	11	30 25
5 0	8	30 01
	17	30 01
0 0	12	29 51
	15	29 54
	46	29 54
−22 9	3	28 03
	8	28 18
	23	28 31
	34	28 40
	43	28 40

Two series of experiments have been carried out, in the first of which pure monomeride was introduced into the apparatus and the pressure read at various intervals over a period of approximately twelve months. In order to define the compositions giving rise to the above pressure a second series was carried out, in which definite mixtures were made and the pressures measured immediately. This gave a pressure–composition curve,

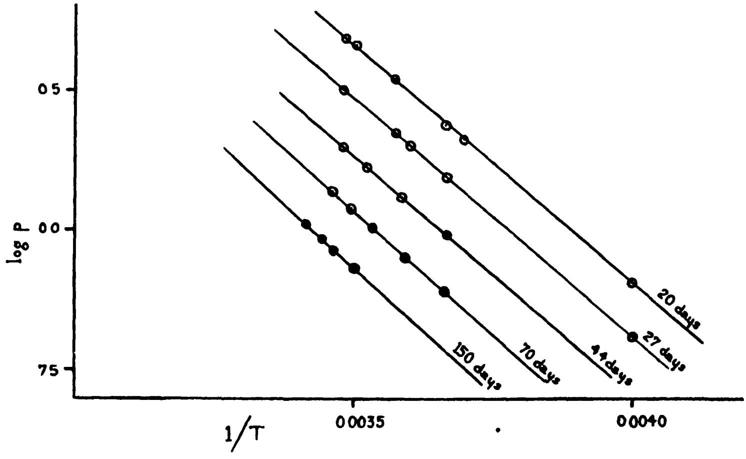

FIG. 2

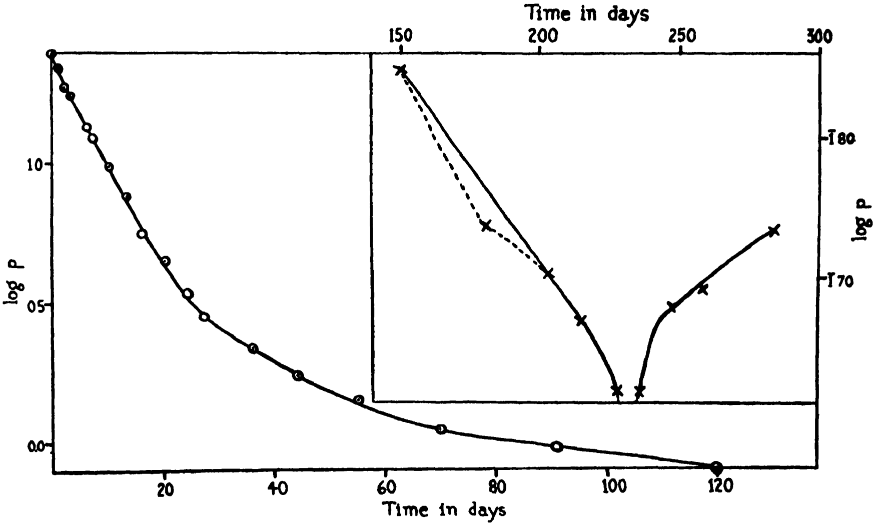

FIG. 3

and hence the pressure–time series could be converted into composition–time readings.

In table 1 the complete readings for the vapor pressure curve on the twenty-seventh day are given, and typical data expressed in figure 2, the pressures being in centimeters of mercury and the time in minutes.

The pressure figures at 12°C. were obtained from the log p: $1/T$ curves and are expressed in figure 3 which shows the change of pressure with time.

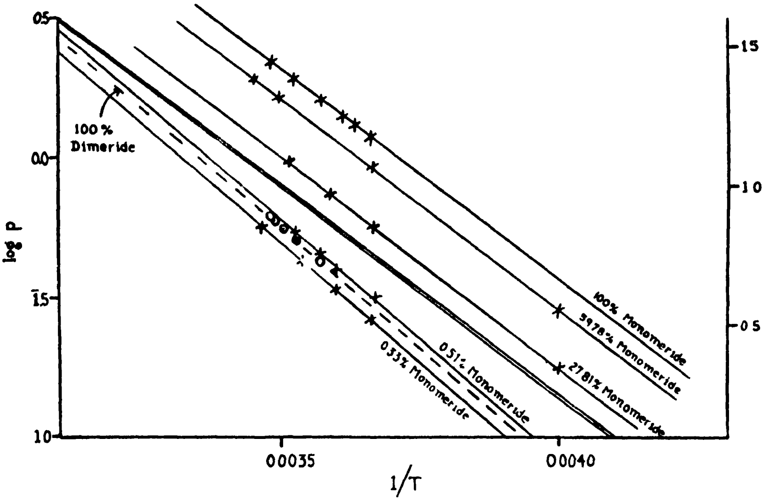

FIG 4

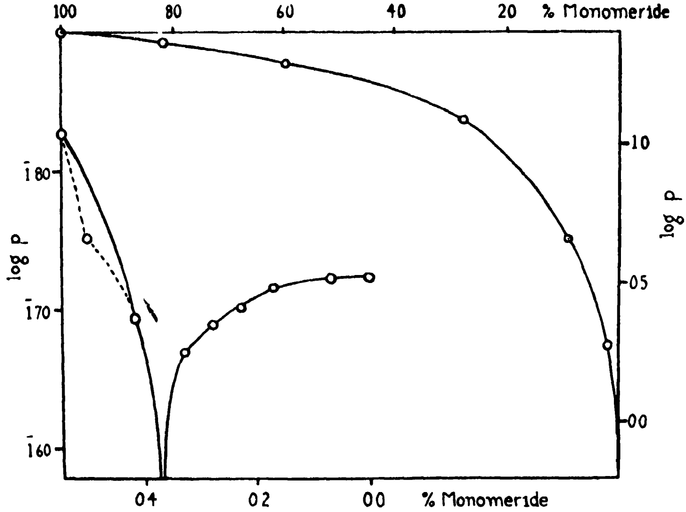

FIG. 5

A selection of curves from the second series is given in figure 4, the values at 12°C. being expressed in figure 5.

It will be seen that the vapor pressure curve passes through a minimum at a composition of approximately 0.36 per cent monomeride. This curve made it possible to calculate the composition at any point on the vapor pressure–time curve and hence the relation between per cent of monomeride and time has been obtained, the data being expressed in figure 6.

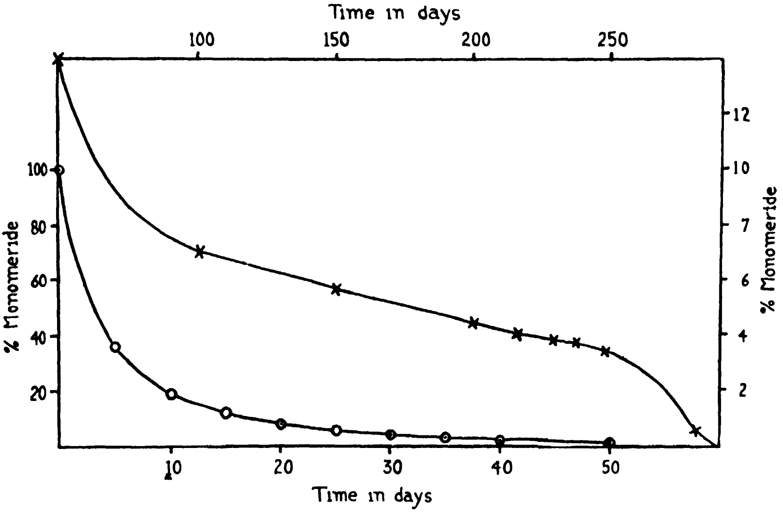

FIG. 6

DISCUSSION

One may regard the polymerization as proceeding for the one stage only (monomeride→dimeride) under the conditions of experiment, since the pressure finally remained constant over a considerable period. The chief point of interest, however, lies in the fact that the dimeride forms liquid crystals. It is now well established that liquid crystals are phases intermediate between the crystalline (solid) and amorphous (liquid) states. G. Friedel (2) considers that there may be two or possibly more such phases between the true crystalline and the true liquid forms. He then states that the order of succession must always be crystalline, smectic (soap-like), nematic (thread-like), liquid, and the reaction goes in this direction with increasing temperature or on dilution.

The present work showed that the dimeride exhibited these properties, for, after 150 days there was an appearance of thread-like bodies in the liquid, the latter becoming considerably more viscous, while after 181 days the solution set to a stiff opalescent jelly. On raising the temperature the reverse process took place. On the 203rd day the container was surrounded with ice for the lowest point, but the pressure obtained was abnormally high. On removing the ice bath it was found that practically the whole of the solution had changed to a crystal mass (dimeride), leaving only a small amount of liquor which was richer in monomeride than should have been the case if the liquid crystals had been present, thus causing the pressure to correspond to a composition of some weeks previously. After this point the 0°C. figure was omitted, the tendency for crystal formation being thereby largely removed. After 229 days the solution became more fluid as it approached the pure dimeride state.

When the solution was fluid equilibrium was rapid, but as soon as liquid crystals had formed it was very slow. The points in figure 2 which were in contact with the smectic mesophase have been marked with solid circles. A survey of the curves showed that the form was the same, whether the solution with which it was in contact was liquid or contained liquid crystals, at any rate to within experimental error over the range measured.

After one year the monomeride had completely changed into the dimeride and there was no evidence from the vapor pressure measurements that the change was proceeding further. At the close of the experiment the liquid had a slight opalescence, but there was no trace of resin formation. However, on exposure to air the liquid turned yellowish in color with distinct rapidity. From this it would appear that only the reaction, monomeride → dimeride, takes place in a vacuum, but that it proceeds to a resin in the presence of air.

It would appear quite probable that the dotted lines in figures 3 and 5 represent the correct curves, since the pressure is about the same amount below the smooth curve in each case, and as one is obtained from the monomeride→dimeride series and the other is the vapor pressure of a definite mixture, this cannot be a chance agreement. On the basis of the phase rule, the two forms of liquid crystal are considered to be distinct phases and will therefore give rise to invariant points on the phase diagram. There are not enough points to show the position of each section of the curve, but the presence of a point so far removed from the smooth curve shows that the latter is discontinuous.

The mesophases would appear to exert a considerable influence on the reaction time curve. For example, reference to figure 6 shows that the amount of monomeride steadily decreases up to a period of 93 days, at which point approximately 0.73 per cent remains. From this point up to a period of 235 days the curve is almost linear, and represents an extremely slow rate. From 235 days onwards, however, the change is again much more rapid. Between the two periods mentioned the liquid phase contained liquid crystals, and hence, the reason for the slow rate of change over this period may be due to hindrance to diffusion of the molecules in the solution, owing to the resistance occasioned by the presence of these liquid crystals.

SUMMARY

1. The vapor pressure of a cyclopentadiene has been measured at various temperatures during the change from 100 per cent monomeride to 100 per cent dimeride.

2. The vapor pressures of known mixtures of monomeride and dimeride have been determined at various temperatures.

3. The formation of liquid crystals has been observed and the conditions noted.

The authors with to express their thanks to Professor A. J. Allmand for the interest that he has taken in this work.

REFERENCES

(1) CHAPLIN: Proc. Roy. Soc. London **A121**, 344 (1928).
(2) FRIEDEL: Ann. phys. [9] **18**, 273 (1922).

THE RATE OF BROMATE FORMATION IN AQUEOUS SOLUTIONS CONTAINING HYPOBROMOUS ACID AND ITS ANION

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In connection with other kinetic investigations, we have found it convenient to prepare aqueous solutions containing hypobromous acid by adding bromine to a phosphate buffer solution containing silver ion;[1] as hydrogen ion and bromide ion are rapidly removed, the hydrolysis equilibrium of bromine is shifted,

$$Br_2 + H_2O \rightarrow HBrO + H^+ + Br^- \qquad (1)$$

and the concentration of hypobromous acid is increased. Although the rate laws given by Skrabal and Weberitsch (1) for the reaction[2]

$$5HBrO = BrO_3^- + H^+ + 2Br_2 + 2H_2O \qquad (2)$$

indicate that[3] (HBrO) in our solutions should decrease to half its value in, say, 10^{-2} seconds, we found that approximately twenty-four hours elapsed before so much decomposition occurred. Duplication of part of the work of Skrabal and Weberitsch has convinced us that their results are entirely reliable, and that the source of this surprising conflict must consequently be sought in their interpretation of these data. We have concluded that much of the conflict has resulted from several errors, which we shall point out, and that our preliminary rate measurements, some twenty in number, indicate how the mechanism of reaction 2 may be directly investigated. We have no intention at present of undertaking a further investigation ourselves.

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[1] After several unsuccessful attempts to prepare aqueous solutions containing only hypobromous acid by the distillation methods recommended in the older literature led us to conclude that this could not be accomplished, we discovered that Pollak and Doktor (Z. anorg. allgem. Chem. **196**, 89 (1931)) had already reached this conclusion as a result of similar experiments.

[2] The stoichiometric equation for the formation of bromate ion will assume different forms under different experimental conditions BrO^-, Br_3^-, or Br_2 may appear as reactant instead of HBrO, and what substances, in addition to BrO_3^-, appear as resultants is also subject to change. Decomposition of bromine compounds to yield oxygen is negligible under all experimental conditions with which we have here to deal.

[3] As in other communications, the following conventions will be observed: ( ) means "concentration of" in moles per liter; the units for all specific rates are moles, liters, minutes; when no temperature is specified, 25°C. (or nearly 25°C.) is meant; → will be restricted to steps which may be rate-determining. Rate laws will usually be referred to by letter only; the proper letter used as subscript will indicate to which law a specific rate constant belongs.

In table 1 are summarized the rate laws that should govern the stability of hypobromous acid in all solutions not strongly alkaline. We shall now consider evidence to show that C (or C′) is more plausible than B (or B′), that A is not experimentally established, and that the kinetic data upon which table 1 is based can be interpreted in terms of the rate-determining step

$$2HBrO + BrO^- \rightarrow BrO_3^- + 2H^+ + 2Br^- \qquad (3)$$

given by Kretzschmar (2). (The intimate mechanism of this rate-determining step will be discussed later)

To secure data that may aid in deciding the relative plausibility of B′ and C′ (or, of B and C) we have measured the stability of hypobromous acid in phosphate buffer solutions at the low (Br^-) insured by the presence of Ag^+. These experiments, given in table 2, together with all others in which the rate of disappearance of hypobromous acid was measured, were carried out as follows. The reaction mixture, contained in a glass-stoppered flask and shielded from direct sunlight, was placed in a thermostat at 25°C. At convenient intervals samples were withdrawn, run into an iodide solution containing $H_2PO_4^-$, and titrated with 0.004 *N* thiosulfate. Calculations and blank tests concurred in showing that the bromate present was not reduced rapidly enough under the conditions employed to cause any error in the titration.

The experimental results in table 2 agree in order of magnitude with the rates calculated from C′--but not at all with those from B′. Further, the actual rate at which hypobromous acid disappears under the above conditions is (virtually) *independent* of (Br^-), in agreement with C′ but not with B′. Our experimental evidence, joined to that of Skrabal and Weberitsch (X, Versuche 11 to 14 inclusive), has convinced us that of the two rate laws C′ is far the more plausible. We must admit, however, that the proof is not complete; for, as will appear later, extension of the results in table 2 has not permitted the deduction of a definite rate law.

Skrabal and Weberitsch were led to adopt B because this differential equation, when properly combined with that for the reduction of bromate by bromide ion in acid solution, gave the equilibrium constant for reaction 2 (X, pp. 249–52); we are not certain that this agreement between a quotient of specific rates and an equilibrium constant warranted changing

TABLE 1

Summary of rate laws for reaction 2

These laws are intended to govern $-d\Sigma(Br_2)/dt$ except in strongly alkaline solutions; $\Sigma(Br_2) = (Br_2) + (Br_3^-) + (HBrO)$

RATE LAW	SPECIFIC RATE AT 25°C.	CONCENTRATION TERMS	REFERENCE	COMMENT
A	$6.5(10^4)$	$\frac{(OH^-)(Br_3^-)^2}{(Br^-)^3}$	X,* p. 244 et seq.	Adopted for their "rapid reaction" by S. and W.
B	$8\ 3(10^{22})$†	$\frac{(OH^-)^4\,(Br_3^-)^3}{(Br^-)^7}$	X, p 246 et seq.	Adopted for their "slow reaction" by S. and W.
B′	$2\ 7(10^9)$†‡	$\frac{(HBrO)^3\,(OH^-)}{(Br^-)}$		Alternative form‡ of B
C	$2.4(10^{23})$†	$\frac{(OH^-)^4\,(Br_3^-)^3}{(Br^-)^6}$	As for B	Given directly by the experimental evidence. Not adopted by S. and W. because they considered B more plausible.
C′	$7\ 9(10^9)$†‡	$(HBrO)^3\,(OH^-)$		Alternative form‡ of C
C″	Definite value cannot be given	$(HBrO)^2\,(BrO^-)$	Kretzschmar (2)	Alternative form§ of C

* See reference 1.

† We have calculated these specific rates from Versuch 14 (X, p. 248), employing for this purpose the correct concentrations: namely, $(Br_3^-) = 0.059$ and $(Br^-) = 0.34$. In their calculations, Skrabal and Weberitsch assumed (mistakenly) $(Br_3^-) = \Sigma(Br_2) = 0.07$, and obtained $k_B = 3.8(10^{22})$; the difference between this and $8.3(10^{22})$, which corresponds to the correct concentrations, serves to emphasize how sensitive are specific rates involving high orders to relatively small concentration changes.

Versuche 11, 12, and 13, for which Skrabal and Weberitsch did not evaluate k_B, give for $k_C(10^{-23})$, respectively, 1.9, 3.9, and 2.3; these, together with the value $2.4(10^{23})$, given above, show what concordance may be reasonably expected from such measurements.

‡ B and B′ are alternative forms of one rate law, C and C′ of another, for the equilibrium

$$HBrO + 2Br^- \rightleftharpoons Br_3^- + OH^- \qquad (4)$$

is always maintained; the value of its equilibrium constant, the cube of which is involved in each transformation, is (X, p. 245; see reference 1)

$$\frac{(Br_3^-)\,(OH^-)}{(HBrO)\,(Br^-)^2} = 3.2(10^{-5}) \text{ at } 25°C.$$

§ The identity of C′ and C″ is made obvious by writing

$$(BrO^-) = 1/K_{hyd.}(HBrO)\,(OH^-)$$

the uncertainty in the value of $K_{hyd.}$ precludes giving an exact value for $K_{C''}$.

the experimentally derived halide term[4] in C to that in B. We wish to emphasize that the specific rate of reaction 3 need stand in no simple relation to the equilibrium constant of reaction 2.

The experimental evidence in X (see reference 1) upon which A is based involves Versuche 5, 6, and 7 (Versuche 8, 9, and 10 deal with the influence of electrolytes); of these, Versuch 6 is used in the calculation of the specific rate. In this calculation (X, p. 244) there is implicit the assumption that the rate due to C′ (or to B′) is *negligible*. At $t = 15$, $-d\Sigma(Br_2)dt$ in Versuch 6 was $1.4(10^{-4})$ moles per minute per liter; from C′ we calculate a corresponding rate, in these units, of $114(10^{-4})$; and from B′, of $39(10^{-4})$; these calculations may be verified by use of the data in table 3. The magnitudes of these rates leave no doubt that C′, which we have adopted as more plausible than B′, must be considered in the interpretation of these data; indeed, they suggest that all the observed rate in Versuch 6 may be due to reaction 3, for which C′ is one form of the rate law.

TABLE 2

Rate of disappearance of hypobromous acid in potassium phosphate buffer solutions at $(HBrO) = 5(10^{-4})$

EXPERIMENT	$(OH^-)10^8$*	$(Br^-)10^9$†	RATES IN MOL B′	C′	Measured
8	0.67	1	2.2×10^8	0.66	2.2
19	1.15	1.2	3.3×10^8	1.1	19
15	4.8	2.6	6.2×10^8	4.7	46
17	19.6	5.2	12.7×10^8	19	71
6	47	4.3	37×10^8	46	21
7	47	13×10^4	12×10^2	46	13
5	52	7×10^5	2.5×10^4	51	17

* (OH^-) was calculated from the data given by Cohn (J. Am. Chem. Soc. **49**, 173 (1927)); we need not distinguish between (OH^-) and its activity. In experiments 5, 6, 7, and 8, total phosphate was 0.05 *M*, in the others, 0.2 *M*.

† Values of (Br^-) are approximate; except in experiments 5 and 7, silver bromide and (usually) silver phosphate were present as solids; in these cases, (Br^-) was calculated from $(Ag^+)(Br^-) = 5.3(10^{-13})$ and (when necessary) from $(Ag^+)^3(PO_4^{---}) = 1.6(10^{-18})$

And this suggestion becomes more plausible when we observe the constancy of k_3 in Versuch 6, a constancy also found in Versuche 5 and 7. (We do not believe that k_2 is, in any of these experiments, sufficiently constant to permit the valid derivation of a rate law.) Even if we adopt k_3, and thus the $(Br_3^-)^3$ term, we have yet to show that the rate obeys not the (OH^-) and $1/(Br^-)^3$ terms in A, but the $(OH^-)^4$ and $1/(Br^-)^6$ terms in C. We observe next that the orders given in A for these concentrations were not correctly calculated, and for this reason: They were obtained from the effects on k_2 of changing (OH^-)—Versuche 5 and 6— and Br^-—Versuche 5 and 7. But k_2 involves

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[4] We have duplicated Versuche 11 and 14 (X, p. 247) and found $1/(Br^-)^{6.1}$ for the halide term; Skrabal and Weberitsch obtained $1/(Br^-)^{5.8}$.

$$\Sigma(Br_2) = (HBrO) + (Br_2) + (Br_3^-)$$

Manifestly, altering either (OH^-) or (Br^-) will alter the distribution of $\Sigma(Br_2)$ among these three terms (cf. reaction 4); if at least two of these are of appreciable magnitude, this change in distribution will be reflected in the rate; in comparing values of k_2 from two experiments designed to determine the order with respect to some reagent, this change must be considered, or an erroneous result will be obtained. We have allowed for this change in calculating the orders given in table 4, in which a comparison of the seventh and eighth columns will reveal the importance of considering the distribution of $\Sigma(Br_2)$. (See also the last four columns in table 3.)

TABLE 3

*Recalculation of Versuch 6**

$(OH^-) = 2.1(10^{-5})\ M$; $(Br^-) = 1.0\ M$

t	$(Br_2)10^3$	$(Br_3^-)10^3$	$(HBrO)10^3$	k_2†		k_3†	
				S and W	Corrected	S and W	Corrected
0	0.50	8.15	5.30				
15	0.39	6.32	4.11	1.36	3.93	112	549
30	0.33	5.35	3.47	1.10	3.18	112	549
75	0.24	3.90	2.49	0.90	2.60	116	568

* X, p 241 cf also X, p 244

† The units for all specific rates are moles, minutes, liters (To express the specific rates in X in these units, the k_2 given there must be multiplied by $2(10^3)$, and the k_3 by $4(10^6)$)

The "S and W." rate constants are defined by

$$-\frac{d\Sigma(Br_2)}{dt} = k_2\Sigma(Br_2)^2 = k_3\Sigma(Br_2)^3$$

The "corrected" rate constants are defined by

$$-\frac{d\Sigma(Br_2)}{dt} = k_2(Br_3^-)^2 = k_3(Br_3^-)^3$$

at constant (OH^-) and (Br^-)

The terms $(OH^-)^{3.7}$ and $1/(Br^-)^{5.9}$ are in satisfactory agreement with those to be expected from C. Taken by themselves, the results in table 4 are as good evidence for C as can be adduced from any other experimental work in X; for the k_C values in table 4 agree as well among themselves as do those from the phosphate buffer solutions (cf. table 1, footnote†). The average of the latter, 2.4 (10^{23}), is some seventyfold greater than 3.5

(10^{21}), the mean of the values in table 4; we hesitate to ascribe all this difference to equilibrium salt effects, although these will be unusually large in the reaction system with which we are dealing. (If the rate-determining step, reaction 3, is correct, the $1/(Br^-)^6$ term, to give one example, will be due entirely to equilibria preceding this step; such a state of affairs makes for large salt effects.) Nevertheless, we have concluded that there is evidence in X for only one rate law, C, for which the rate-determining step is reaction 3; the numerical value of the corresponding specific rate is uncertain.

TABLE 4

*Carbonate-bicarbonate buffer solution experiments used to establish rate law A**

VERSUCH	Br^-	$(Br_2)10^3$	$(Br_3\ )10^3$	$(HBrO)10^3$	$(OH\ )10^5$	k_3† S and W	k_3† Corrected	$k_C(10^{-21})$	$k_C'(10^{-5})$
5	1 0	0 58	9 41	3 01	1 04	16	42 3	3 8	1 24
6	1 0	0 33	5 35	3 47	2 08	113	552	3 0	0 97
7	0 51	0 31	2 53	3 16	1 04	188	2520	3 8	1 24

Variation of k_3 with (OH^-): From Nos. 5 and 6: $\frac{552}{42\ 3} = \left[\frac{2.08}{1.04}\right]^x$; $x = 3.7$. Rate $\propto (OH)^{3.7}$

Variation of k_3 with ($Br\ $)· From Nos 5 and 7: $\frac{2520}{42.3} = \left[\frac{1\ 0}{0\ 51}\right]^y$; $y = 5.9$. Rate $\propto \frac{1}{(Br^-)^{5\ 9}}$

* X, p. 241

† Cf. footnote†, table 3. In our definition of $\Sigma(Br_2)$, (BrO^-) has been omitted. In justification of this procedure we mention that it is simplest, and that (BrO^-) cannot be calculated until the dissociation constant of HBrO is known. We observe that considering (BrO^-) tends to increase both k_C and the orders obtained for (OH^-) and $1/(Br^-)$: thus, assuming $K = \frac{(H^+)(BrO^-)}{HBrO} = 10^{-9}$, gives $(OH^-)^{5\ 3}$ and $1/(Br^-)^{7.1}$, while assuming $K = 10^{-10}$ scarcely changes the results in table 4. Since the assumption of the larger value leads to no simple kinetic conclusions, we have preferred omitting (BrO^-) from consideration, a procedure tantamount to assuming for K a value of 10^{-10}, or less. If our kinetic interpretation of the data in table 4 is correct, further experiments of the same sort over a range of OH^- concentrations may provide a way of obtaining the dissociation constant of HBrO from kinetic data.

Kretzschmar (2) in 1904 completed the first extensive kinetic investigation of reaction 2. He presents kinetic evidence (reference 2, pp. 794–8) for reaction 3 as a rate-determining step; this interpretation he considers plausible because reaction 3 is analogous to the rate-determining step found by Foerster and Jorre (3) for the formation of chlorate ion through the decomposition of hypochlorous acid. Kretzschmar made rate measurements on solutions of hypobromous acid, prepared by distillation, to which had been added a known amount of potassium hydroxide; he assumed that one mole of added base yielded one mole of hypobromite ion. His measurements give for C a specific rate of approximately $3(10^{19})$,[5] which is to be compared with the values $2.4(10^{23})$ (phosphate buffer) and $3.5(10^{21})$ (carbonate–bicarbonate buffer) obtained from the measurements of Skrabal and Weberitsch. In explaining why Kretzschmar obtained such low values for k_C, two things, in addition to salt effects, must be considered: first, our experience indicates that his hypobromous acid solutions probably contained (H^+) at an appreciable, though unknown, concentration; and second, when base is added to an hypobromous acid solution the amount of BrO^- formed depends upon the dissociation constant of this acid, which is not definitely known.

Our review of the rate laws in table 1 is now complete and leads to this conclusion: Over a wide range of experimental conditions, the law that governs the rate of reaction 2 is formally identical with C″, as found by Kretzschmar (2), and assumes more complex forms (e.g., C) as the composition of the reaction mixture changes. We observe that one form (C″) of this law is analogous to that found by Foerster and Jorre (3) for hypochlorous acid solutions, while another (C) corresponds to one found by Skrabal (4) for the formation of iodate ion. It appears, therefore, that the law

$$-d\Sigma(X_2)/dt = k(HXO)^2(XO^-) \qquad (5)$$

is of general importance in the formation of the halate ion, XO_3^-, through the decomposition of these lower-valent halogen compounds. This law obviously suggests

$$2HXO + XO^- \rightarrow XO_3^- + 2X^- + 2H^+ \qquad (6)$$

as a rate-determining step; when we come to consider, however, what the intimate mechanism of reaction 6 might be, we are faced with several possibilities, of which none can be definitely eliminated. That reaction 6 is trimolecular—i.e., that it involves only triple collisions—seems very improbable; and this justifies the assumption that an equilibrium is involved. The compound $X_3O_2^-$, which has been postulated by Skrabal (4) and favored by Bray (5), may be assumed; but the mechanism

$$\text{Equilibrium: } 2HXO + XO^- \rightleftharpoons X_3O_2^- + H_2O \text{ (or } H_2X_3O_3^-) \qquad (6a)$$
$$\text{Rate-determining: } X_3O_2^- + H_2O \rightarrow XO_3^- + 2X^- + 2H^+ \qquad (6b)$$

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[5] Kretzschmar's data give $k_{C''} = 100$ at 25°C. (cf. reference 2, p. 798); to convert them to our units, his specific rates must be multiplied by 400. If 10^{-10} is assumed to be the dissociation constant of hypobromous acid (this corresponds to a hydrolysis constant for BrO^- of 10^{-4}), then $k_{C'} = 100/10^{-4}$, or 10^6; and $k_C = 10^6/[3.2(10^{-5})]^2$, or $3(10^{19})$.

does not exhaust the possibilities. No matter what mechanism is chosen, however, the simplest procedure, and therefore most logical so long as no conflict with experiment is involved, will be to consider it valid for all the halogens.

Kretzschmar (reference 2, pp. 790–3) also measured the rate of decomposition of hypobromite solutions, which proved to be surprisingly stable. He attempted no kinetic evaluation of these results, but he considered the mechanism

$$3\mathrm{BrO} \rightarrow \mathrm{BrO_3^-} + 2\mathrm{Br^-} \qquad (7)$$

not improbable. In most of his experiments the concentration changes are not appreciable enough to permit the certain deduction of a mechanism; for Uebersicht 3, however, we have found that the rate law is[6]

$$-\frac{d(\mathrm{BrO}^-)}{dt} = 0.056\ (\mathrm{BrO^-})^2 \text{ at } 80°\mathrm{C}. \qquad (8)$$

corresponding to the rate-determining step

$$2\mathrm{BrO} \rightarrow \mathrm{BrO_2^-} + \mathrm{Br^-} \qquad (9)$$

Assuming that this rate law is valid also in the experiments at lower temperatures, we have calculated that the rate of reaction 9 at any temperature is given by

$$-\frac{d(\mathrm{BrO^-})}{dt} = 10^{14}\, e^{-\frac{2.5(10^4)}{RT}}\ (\mathrm{BrO^-})^2 \qquad (10)$$

Within the experimental error, which is rather large,[7] the Arrhenius constant of reaction 9 is identical with the collision number. (10^{13} moles per liter per minute is the collision number for a bimolecular gas reaction at unit concentration of the reactants.) The stability of these hypobromite solutions might be utilized in the preparation of hypobromous acid.

Equation 8 is formally identical with the rate law found by Foerster and Dolch (6) to govern the stability of hypochlorite solutions, and this circumstance is additional evidence for our interpretation of Kretzschmar's results. From the data given by Foerster and Dolch for 25, 50, and 90°C., we have calculated that the rate of the reaction[8]

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[6] The specific rate was calculated for $(\mathrm{OH^-}) = 1.89$; in such basic solutions, (HBrO) is probably negligible, for the rate is (virtually) independent of $(\mathrm{OH^-})$. Since the change in $(\mathrm{Br^-})$ that took place during the experiment was not reflected in the rate, we conclude that $(\mathrm{Br^-})$ does not belong in the rate law.

[7] We estimate the error in the heats of activation in equations 10 and 12 to be ±2000 calories· there is, of course, a corresponding uncertainty in the values of the Arrhenius constants.

$$2ClO^- \rightarrow ClO_2^- + Cl^- \qquad (11)$$

at any temperature is given by

$$-d(ClO^-)/dt = 10^{12}\, e^{-\frac{2.5(10^4)}{RT}}\, (ClO^-)^2 \qquad (12)$$

Although the experimental error is rather large, there is no doubt that the analogous reactions 9 and 11 have almost identical Arrhenius constants and heats of activation.

We shall close with a brief discussion of our rate measurements. Although the rate was followed until nearly all the HBrO had disappeared in some twenty reaction mixtures like those of table 2, no definite order could be established either for (HBrO) or for (OH^-); the one most nearly obeyed with respect to (HBrO) is the second; with respect to (OH^-), the order is not higher than the first. Under some conditions the second order constant with respect to (HBrO) decreased as the run progressed, often it increased, and sometimes it remained unchanged. In all probability we are dealing here with a mixture of reactions, and a change of temperature or of (OH^-) might do much to simplify matters. At any rate, the fact that the rates we measured are independent of (Br^-) leaves little doubt that the rate at which HBrO decomposes into bromate is being measured directly, i.e., that no equilibria are maintained in front of the rate-determining steps. In addition to reaction 3, a second step of the type

$$HBrO + HBrO_2 \rightarrow BrO_3^- + 2H^+ + Br^- \qquad (13)$$

may be involved.

SUMMARY

1. In agreement with the results of Pollak and Doktor (7), it has been found impossible to prepare, by distillation, aqueous solutions containing only hypobromous acid.

2. At low (Br^-), solutions of HBrO are far more stable than one law given by Skrabal and Weberitsch (1) for the rate of the reaction

$$5HBrO = BrO_3^- + 2Br_2 + H^+ + 2H_2O \qquad (2)$$

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[8] At low (OH^-) the rates measured by Foerster and Dolch were independent of (OH^-) and, within limits, of (Cl^-), which nearly doubled in magnitude as some of their experiments progressed (cf. Uebersicht 1, reference 6, p. 140). We see no reason for doubting the plausibility of the above mechanism (in this connection cf. reference 6, p. 144).

allows; a reëxamination of their kinetic evidence has led to the conclusion that, except in strongly alkaline solution, the rate of reaction 2 should be governed by

$$-d\Sigma(Br_2)/dt = k_{C''}(HBrO)^2\,(BrO^-)$$

(At 25°C., widely different values, ranging from approximately 10^2 to nearly 10^6, have been obtained for $k_{C'}$ under different experimental conditions.) In this, its simplest form, the rate law is identical with that found by Kretzschmar (2); further, it appears not irreconcilable with the stability we have observed in our hypobromous acid solutions.

3. Since this rate law is analogous to those found for the formation of ClO_3^- and IO_3 under certain experimental conditions, it has been concluded that the rate-determining step

$$2HXO + XO^- \rightarrow XO_3^- + 2X^- + 2H^+ \tag{6}$$

is of general importance in the formation of halate ions through the decomposition of the halogens (or substances in equilibrium with them).

4. The intimate mechanism of the rate-determining step, reaction 6, cannot be definitely settled; an intermediate compound, like $X_3O_2^-$, in equilibrium with HXO and XO (and, consequently, with X_3 , X_2, and X^-) may be involved, for reaction 6 is probably not the result of triple collisions alone.

5. From the measurements of Kretzschmar (2) in strongly alkaline solution, we have deduced the rate law

$$-d(BrO^-)/dt = 0.056(BrO^-)^2 \text{ at } 80°C. \tag{8}$$

corresponding to the rate-determining step

$$2BrO^- \rightarrow BrO_2^- + Br^- \tag{9}$$

which is analogous to that found by Foerster and Dolch (6) in ClO^- solutions. Reaction 9 and its ClO^- analogue have nearly identical heats of activation and Arrhenius constants.

6. Our rate measurements, as well as those of Pollak and Doktor (7), on reaction 2, indicate a need for further work, which we have no intention at present of undertaking.

REFERENCES

(1) Skrabal and Weberitsch: Monatsh. **36**, 237 (1915). This paper is the tenth of a series and will be designated by X. Papers III and IV also deal with reaction 2.

(2) Kretzschmar: Z. Elektrochem **10**, 789 (1904).

(3) Foerster and Jorre: J. prakt. Chem. **59**, 53 (1899).

(4) Skrabal: Monatsh. **32**, 815 (1911).

(5) Bray: J. Am. Chem. Soc. **52**, 3580 (1930).

(6) Foerster and Dolch: Z. Elektrochem. **23**, 137 (1917).

(7) Pollak and Doktor: Z anorg. allgem. Chem. **196**, 89 (1931).

III. THE EFFECT OF THE ALKALI AND THE ALKALINE EARTH IONS ON THE ADSORPTION OF THORIUM B BY SILVER BROMIDE CRYSTALS

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INTRODUCTION

In previous studies of the relative adsorption of a series of similar ions on polar crystal surfaces, attention has been given to the variable surface of the crystals and to the effects of the addition of foreign ions. In the early work the precipitates were formed in the presence of the material to be adsorbed, thereby introducing such errors as (1) variable surfaces of the precipitates, (2) occlusion of the adsorbed material, and (3) effects due to the presence of the ions formed as by-products in the precipitation reaction.

Fajans (1) in his recent work used carefully dried powders and added radioactive ions as nitrates and the other anions and cations as nitrate and potassium salts. The value of such studies in the field of adsorption is in the possibility of formulating a theory based on quantitative data from observations made on the simplest possible system. Even with the simple systems used by Fajans and others, complications arise. For instance, in the study of the adsorption of thorium B, the simplest possible system may consist of silver iodide crystals in contact with a solution containing as many ions as ThB^{++}, Ag^+, I^-, H^+, OH^-, NO_3^-, Br^-, K^+, and ions from the glass vessels. Then there is the possibility of the adsorption of the thorium B on the walls of the glass vessels and the complications introduced by the formation of other substances by the interaction of the ions listed.

Silver bromide crystals in contact with a solution of potassium bromide acquire a negative charge due to the adsorption of bromide ions. This charge can be shown by a simple cataphoresis experiment or by measuring the amount of the positively charged ThB^{++} ions which can be adsorbed from the solution. Increasing the concentration of the potassium bromide in the solution increases the charge on the crystals and increases the amount of the thorium B adsorbed. Qualitatively, we can say that the additional bromide ions on the surface of the silver bromide crystals mean an increased adsorption of thorium B, but in measurements of the per cent adsorption versus concentration of potassium bromide in solution, we are dealing not only with changing concentrations of ThB^{++} ions and Br^- ions but also with changing concentrations of potassium ions. It is true that, according to the adsorption rule that an ion will be adsorbed if it forms an insoluble compound with the oppositely charged ions of the crystal, very little adsorption of potassium ions would be expected. However, it has been shown (2) that a large concentration of an ion forming a soluble compound with the oppositely charged ion of the crystal will repress from the surface of a crystal adsorbed ions which form very much less soluble compounds. In other words, all ions possess some tendency to be adsorbed or attracted to the surface of a polar crystal. It is only, then, by studying behaviors of different ions alone and in the presence of each other that an accurate adsorption rule can be formulated.

In this work we are interested in the amount of adsorption of thorium B by silver bromide crystals in the presence of varying concentrations of bromide ions and in the part played by the cation of the bromide salt used. Fajans and Erdey-Grúz (3) observed that whereas potassium bromide decreased the amount of erythrosin adsorbed on silver iodide, potassium chloride increased it. King and Pine observed that whereas potassium bromide increased the amount of thorium B adsorbed on thallium iodide, potassium chloride decreased it. The explanation can be given in both cases that this is due to the potassium ions. If potassium ions are changing the charge on the adsorbent, or replacing the adsorbed material from the surface of the adsorbent or being adsorbed along with the material whose concentration is being measured, then there should be certain properties of the potassium ion which determine the part it plays and whose effect can be measured. In this event, if the bromide ion concentration is kept constant and the potassium ion concentration is varied, or if the potassium ion is replaced by another cation, some information about these properties should be obtained. In this paper will be reported the data which was gathered from the measurements made on the adsorption of thorium B on silver bromide from solutions of varying concentrations of the different alkali and the alkaline earth ions.

PREPARATION OF MATERIALS

The water used was made in the same way as that used in the work by King and Pine (1).

Silver bromide

The silver bromide powder used for all the work was prepared according to the method of J. Walker (4). "Tested Purity" silver bromide was dissolved in C.P. ammonium hydroxide (specific gravity 0.9) and then reprecipitated by diluting the ammonia solution with water. Ten liters of the ammonium hydroxide were placed in a 12-liter balloon flask and saturated with the silver bromide by stirring and warming. The solution was then allowed to stand at room temperature, and 100 cc. of the clear solution was run into 400 cc. of water with constant mechanical stirring. The precipitate was allowed to settle and collected by decanting the supernatant liquid. A large amount of precipitate was collected and placed in the washing tower as described in the work of King and Pine. This was washed with stirring continuously, the water being made by distillation in the Barnstead still and run through Pyrex tubing through the wall of the dark room. It was dried in an electric oven at 115°C. and then stored over phosphorus pentoxide in a desiccator. All work with the silver bromide was done in the dark room, using Eastman safelights for illumination.

Bromide salts

The solutions of C.P. or T.P. salts were standardized gravimetrically by precipitating silver bromide or volumetrically against standard silver nitrate, using potassium chromate as an indicator.

The rubidium bromide was Eimer and Amend's "Tested Purity" grade and the cesium bromide was specially prepared here in the laboratory by Professor Mears.

The radioactive solutions were prepared as described in the work of King and Pine and the method of measurement was the same as that used in the work of King and Romer (5).

METHOD OF PROCEDURE

The glassware had the same attention as that used in the work by King and Pine. The pure silver bromide powder was weighed into brown bottles in the dark room. Samples weighing 0.5000 ± 0.0002 g. were used. The correct amounts of acid (see section 6), bromide salts, and nitric acid solution of thorium B were added and the mixture was shaken for 45 minutes. After the settling of the precipitate or after centrifuging, a 5-cc. sample of the supernatant solution was taken for evaporation and activity measurement. Along with each series of measurements was carried a blank or control experiment which was made use of in calculating the per cent of adsorption.

EXPERIMENTAL RESULTS

1. Time of shaking

To find how long a shaking period was necessary to establish adsorption equilibrium, an experiment in which the time of shaking varied was carried out. The results are given in table 1.

From the figures in table 1 it is evident that a shaking period of 30 minutes is ample to establish equilibrium. In the following work, solutions were shaken for 45 minutes.

2. Change in surface of adsorbent

In table 2 are given the results of a series of measurements in which the amount of bromide ion and thorium B is the same but the weight of the silver bromide powder is changed. It is evident from table 2 that ordinary errors in weighing would not appreciably affect the percentage of thorium B adsorbed. Thus if the adsorbent were weighed only to the nearest milligram, the error in the per cent of thorium B adsorbed would not exceed 0.07.

TABLE 1

Time of shaking necessary to establish adsorption equilibrium

0.5 g. of silver bromide; 5 cc. of 0.04 *N* potassium bromide; 10 cc. of water; 10 cc. of nitric acid solution of thorium B

TIME OF SHAKING *minutes*	CORRECTED ACTIVITY *scale divisions per minute*	ADSORPTION *per cent*
Control	39.0	
Control	39.5	
30	13.8	64.9
30	14.0	64.3
60	13.6	65.3
60	13.9	64.5
90	14.2	63.9
90	13.7	65.1

TABLE 2

WEIGHT OF SILVER BROMIDE *grams*	ACTIVITY *scale divisions per minute*	ADSORPTION *per cent*
Control	76.2	
Control	77.7	
0.450	29.8	61.4
0.450	29.7	61.5
0.500	27.7	64.0
0.500	27.1	63.5
0.550	24.9	67.6
0.550	24.3	68.4

3. Effect of light on the adsorption

Five-tenths of a gram samples of silver bromide were used. Samples 3 and 4 in table 3 were handled in the dark room. Samples 5 and 6 were exposed to indirect sunlight for 10 minutes. All other conditions were the same as in previous expériments. We note that an exposure to white light effects our results but slightly. To eliminate errors from this source, however, all operations in the following work, except the final evaporation of the radioactive samples, were carried out in the dark room, using Eastman safelights for illumination.

TABLE 3

Effect of light on the adsorption

	ACTIVITY	ADSORPTION	AVERAGE
	scale divisions per minute	*per cent*	
Control	99.7		
Control	100.0		
Dark	44.7	55.2	54.7
Dark	45.7	54.2	
Light	43.1	56.8	56.9
Light	42.9	57.0	

TABLE 4

The "holding back" effect of lithium bromide

Concentration of nitric acid = 4 millimoles per liter

SILVER BROMIDE	CONCENTRATION OF LITHIUM BROMIDE	CORRECTED ACTIVITY	APPARENT PER CENT ADSORPTION	PER CENT OF ACTIVITY HELD BACK BY LITHIUM BROMIDE	CORRECTED PER CENT ADSORPTION
gram	*millimoles per liter*	*scale divisions per minute*			
0	0	96.5			
0	0	96.5			
0	0	95.5			
0.5	0	91.3	5.1		5.1
0	8	94.8		1.5	
0.5	8	29.8	69.0		67.5
0	20	94.3		2.0	
0.5	20	20.8	78.4		76.4
0	28	92.0		4.4	
0.5	28	18.2	81.1		76.7
0	40	89.1		7.4	
0.5	40	15.3	84.1		76.7
0	48	87.5		9.0	
0.5	48	13.5	86.0		77.0
0	60	84.2		12.5	
0.5	60.2	12.2	87.3		74.8

4. The "holding back" effect of lithium bromide

Lithium bromide is so hygroscopic that it took up water from the air before the measurements of the activity of the watch glasses containing the active material could be made. In table 4 are given the results using an excess of lithium bromide. In a similar experiment with the other alkali bromides, no "holding back" effect was observed at concentrations of 8 and 16 millimoles per liter. Accordingly, no corrections for this effect were necessary at these concentrations except in the case of lithium bromide.[1]

5. The effect of varying concentrations of thorium B on the adsorption

A study was made of the change of adsorption with a change in the activity of solution. The results are tabulated in table 5. These results, which indicate that the per cent adsorption decreases in solutions of higher ThB^{++} concentration, are in agreement with the general adsorption rule.

TABLE 5

The adsorption of thorium B on silver bromide with varying concentrations of thorium B

0.5 g. of silver bromide; concentration of nitric acid = 6 millimoles per liter; concentration of potassium bromide = 20 millimoles per liter

ACTIVE SOLUTION	CORRECTED ACTIVITY	ADSORPTION	AVERAGE
cc.	*scale divisions per minute*	*per cent*	
5 (Blank)	31.6		
5 (Blank)	31.3		
5	11.5	63.4	63.4
5	11.5	63.4	
10 (Blank)	64.4		
10 (Blank)	64.6		
10	26.6	58.8	59.1
10	26.2	59.4	
15 (Blank)	96.8		
15 (Blank)	96.2		
15	43.5	55.0	55.6
15	42.3	56.2	

6. The effect of hydrogen-ion concentration

A study was made of the effect of different hydrogen-ion concentrations in order to find out what concentration of hydrogen ion would give reproducible adsorptions of thorium B. The data is given in table 6.

It is evident that reproducible results are not obtainable in solutions in which the acid concentration is much less than 4 millimoles per liter. For a discussion of the factors involved, see King and Pine (1). In the following work, the acid concentration in the solutions investigated was held at 4 millimoles per liter.

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[1] Professor Fajans, who is now investigating the cation effect in his laboratory in Munich, in a private communication (September, 1933) stresses the possibility of the introduction of an error in such work by what he calls the "crust effect." He gives his method for the elimination of such an error In all our work attention was given to the formation of the salt crust on the watch glasses used for the activity measurements as described in the paper of King and Pine (reference 1). Where this error was greater than the experimental error, we have corrected for it by means of a control in which the halide salt was used without the silver bromide powder and the same careful evaporation was carried out.

TABLE 6

Effect of hydrogen-ion concentration on the adsorption of thorium B

0.5 g. of silver bromide; concentration of potassium bromide = 4 millimoles per liter

CONCENTRATION OF NITRIC ACID	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
1	146.8	Blank
1	146.8	Blank
1	104.9	28.5
1	126.0	14.2
2	72.5	50.6
2	66.2	54.9
3	78.0	46.9
3	90.9	55.9
4	66.6	54.6
4	68.6	53.3
5	70.3	52.1
5	69.6	52.6
8	77.6	47.1
8	74.4	49.3

TABLE 7

The adsorption of thorium B on silver bromide in the presence of excess sodium bromide and potassium bromide

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION		CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
NaBr	0 (Blank)	71.5	
	0	70.3	1.67
	8	27.0	62.2
	20	17.4	75.7
	28	15.3	78.6
	40	14.2	80.1
	48	12.7	82.2
	60	10.8	84.9
KBr	0 (Blank)	74.9	
	0	72.1	3.7
	8	39.0	47.9
	20	25.0	66.6
	28	22.3	70.1
	40	18.5	75.3
	48	16.9	77.3
	60	16.8	77.5

7. The adsorption of thorium B on silver bromide in the presence of varying concentrations of potassium bromide and sodium bromide

The measurements were made over a large range in concentration of the two alkali bromides. The results are given in table 7.

TABLE 8

Adsorption of thorium B on silver bromide in the presence of excess of the alkali bromides

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION OF ALKALI BROMIDE		CORRECTED ACTIVITY	ADSORPTION	AVERAGE
	millimoles per liter	*scale divisions per minute*	*per cent*	
LiBr	8	56.6	Blank	
	8	56.2	Blank	
	8	15.2	73.2	73.3
	8	15.0	73.4	
	16	53.8	Blank	
	16	54.3	Blank	
	16	11.5	78.6	78.1
	16	12.1	77.6	
NaBr	8	16.3	70.0	70.8
	8	15.4	71.7	
	16	12.8	76.6	76.3
	16	13.0	76.1	
KBr	8	55.0	Blank	
	8	54.0	Blank	
	8	22.4	58.9	61.0
	8	20.1	63.2	
	16	17.7	67.5	67.1
	16	18.1	66.8	
RbBr	8	24.6	54.9	53.8
	8	25.8	52.7	
	16	20.8	61.8	62.4
	16	21.1	63.1	
CsBr	8	33.4	38.7	38.7
	8	33.3	38.8	
	16	29.1	46.6	47.1
	16	28.6	47.6	

8. A study of the effect on the adsorption of all the different alkali bromides a concentrations of 8 and 16 mollimoles per liter

The results are given in table 8 and plotted in the curves in figure 1.

8a. *The effect on adsorption of lithium bromide and cesium bromide at concentrations of 0.1 and 0.01 millimoles per liter*

The data in table 8 represent the results of a study of the adsorption of ThB^{++} on silver bromide in the presence of all the different alkali bromides at concentrations of 8 and 16 millimoles per liter. In table 8a, the results obtained with lithium bromide and cesium bromide at concentrations of 0.1 and 0.01 millimole per liter are given. These results are plotted in the graph of figure 1.

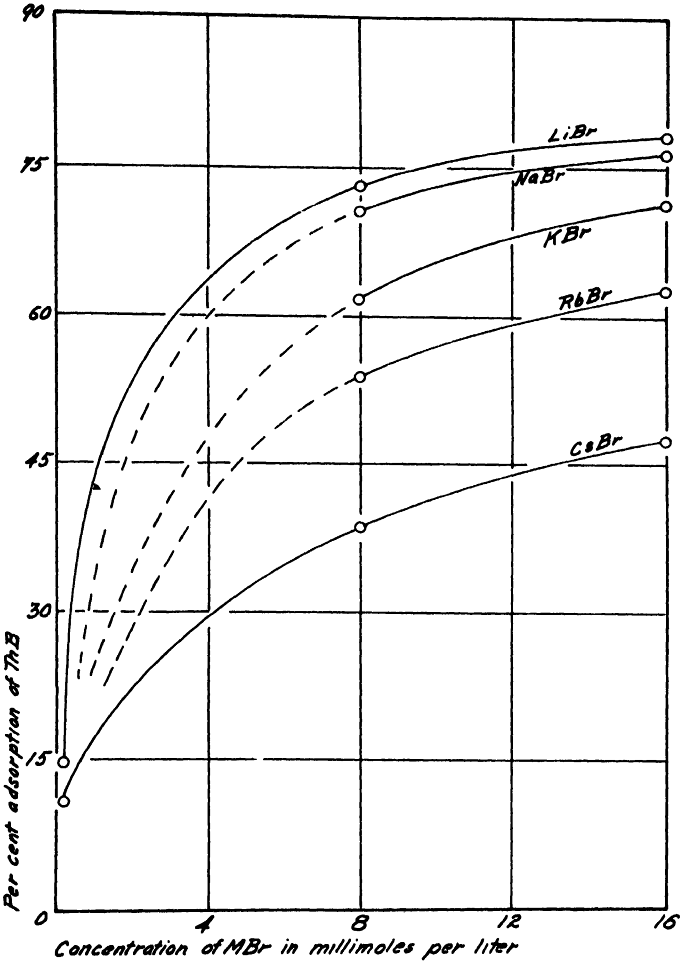

FIG. 1. ADSORPTION OF THORIUM B ON SILVER BROMIDE IN THE PRESENCE OF EXCESS OF THE DIFFERENT ALKALI BROMIDES

TABLE 8a

Adsorption of thorium B on silver bromide in the presence of excess of alkali bromide

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

	CONCENTRATION OF ALKALI BROMIDE	CORRECTED ACTIVITY	ADSORPTION	AVERAGE
	millimoles per liter	*scale divisions per minute*	*per cent*	
CsBr	0.1	88.8	Blank	
	0.1	89.1	Blank	
	0.1	82.4	7.2	10.8
	0.1	75.9	14.5	
	0.01	85.5	3.7	3.1
	0.01	86.6	2.5	
LiBr	0.1	89.0	Blank	
	0.1	88.3	Blank	
	0.1	76.7	13.6	14.8
	0.1	74.5	16.1	
	0.01	85.1	4.2	3.5
	0.01	86.3	2.8	

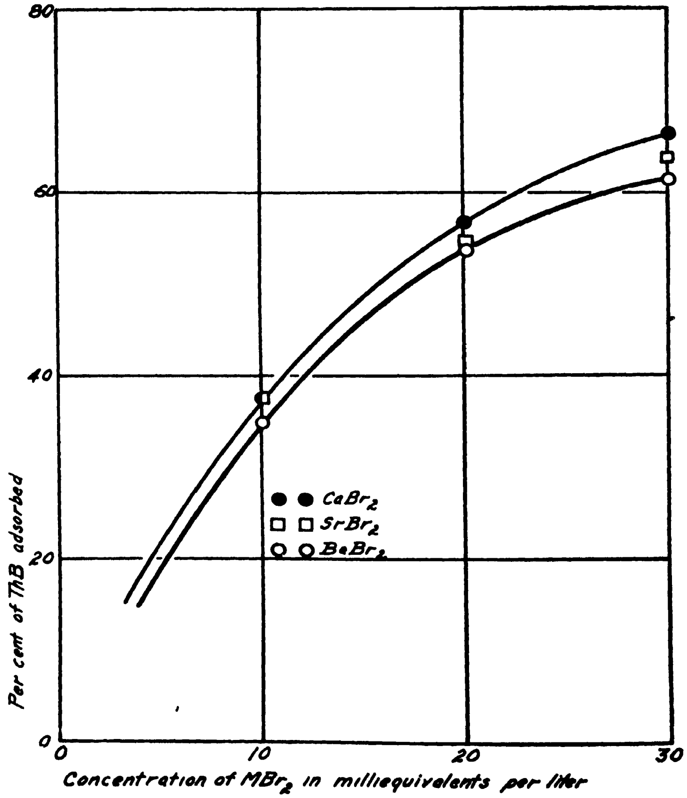

FIG. 2. ADSORPTION OF THORIUM B ON SILVER BROMIDE IN THE PRESENCE OF EXCESS OF ALKALINE EARTH BROMIDES

9. *A study of the effect of the alkaline earth bromides on the adsorption of thorium B by silver bromide*

Because of their hygroscopic properties in all cases a correction was made for the "holding back" effect. The results are given in table 9 and are plotted in the curves in figure 2.

TABLE 9

Effect of the alkaline earth bromides on the adsorption of thorium B on silver bromide

0.5 g of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION OF BROMIDE		CORRECTED ACTIVITY	ADSORPTION
	milliequivalents per liter	*scale divisions per minute*	*per cent*
$CaBr_2$	30 (Blank)	77.3	
	10	48.5	37.3
	20	35.7	53.8
	30	26.1	66.2
$BaBr_2$	30 (Blank)	82.6	
	10	51.9	37.2
	20	37.4	54.7
	30	30.0	63.7
$SrBr_2$	30 (Blank)	83.1	
	10	54.6	34.3
	20	36.1	56.6
	30	32.1	61.4

DISCUSSION

In experiment 7 (table 7) the adsorption of thorium B on AgBrBr particles was measured over a range of concentrations of excess sodium bromide and potassium bromide of from 8 millimoles to 60 millimoles per liter. The adsorption of thorium B is greater for sodium bromide than for potassium bromide throughout the whole range.

In experiments 8 and 9 data were obtained for lithium bromide, sodium bromide, potassium bromide, rubidium bromide and cesium bromide. The order for the repression of the adsorption of thorium B is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ at all concentrations measured. At the very low concentration of 0.01 millimole per liter, the differences observed may be attributed to experimental error.

In experiment 9 (table 9, figure 2), the effects of the three alkaline earth bromides—barium bromide, calcium bromide, and strontium bromide—were measured. There is a very small difference, if any, in the effect of the alkaline earth ions on the adsorption of thorium B by silver bromide.

Since in all of the many series of measurements carried out, all factors were held constant with the exception of the cation to be found in the system at equilibrium, there must be some connection between the order of adsorption and some properties of these cations. We may look on the phenomenon as silver bromide particles negatively charged by the addition of bromide ions selectively adsorbing thorium B from solutions containing the same concentrations of the different alkali and alkaline earth cations. Because thorium B forms a much more insoluble compound with the oppositely charged ion of the silver bromide–bromide particles than do the alkali and alkaline earth ions, it will be much more readily adsorbed. However it has been shown that hydrogen ion, which forms no insoluble compound, may displace the very easily adsorbed ThB^{++} ions from the surface of crystals. It can be expected that all cations behave in some such way. In other words, all ions possess some tendency to be fixed to a polar crystal surface. Therefore, we may use the above data to arrange the cations in the order of their adsorbability on the silver bromide–bromide particles.

TABLE 10

ALKALI ION	PER CENT ADSORPTION OF THORIUM B	HEATS OF HYDRATION	SOLUBILITIES AT 25°C	IONIC SIZE
		calories per gram	*moles per 100 g water*	*A. U*
Li^+.... .	73.3	120	2.09	0.70
Na^+..	70.8	92	0.814	1.00
K^+. .	61.0	72	0.569	1.33
Rb^+..	53.8	68	0.695	1.52
Cs^+. .	38.7	62	0.578	1.70

According to the adsorption theories mentioned in the previous papers, (1) that cation which forms the most insoluble compound will be most easily adsorbed, (2) that cation which is most easily deformable will be most easily adsorbed, and (3) that cation which is least hydrated will be most easily adsorbed. In the first column of table 10 are given the alkali ions in order of their adsorbability as measured by the per cent of thorium B ions adsorbed in 8 millimoles per liter of alkali bromide; in the second column are given the heats of hydration of these cations in calories per gram, which can be used as a measure of the hydration of the ions; in the third column are given the solubilities of the alkali bromides in moles per 100g of water at 25°C; in the fourth column are given the sizes of the cations in Ångstrom units (6).

Fajans (7) has measured the molecular refractivities of the alkali ions to show their deformability. The deformability is in accord with the size, the largest ion being the most easily deformed or polarized in forming a compound.

SUMMARY

1. A study has been made of the adsorption of thorium B ions on silver bromide crystals in the presence of various concentrations of the alkali and alkaline earth bromides.

2. It has been shown that when the bromide ion concentration has been kept constant and the cation has been changed there has been a change in the adsorption of the thorium B ions on the silver bromide crystals due to an adsorption of the cations along with the thorium B ions.

3. There appears to be a relation between the adsorbability of the cations and their heats of hydration, their ionic size and the solubility of their bromide salts.

REFERENCES

(1) See King, J. F., and Pine, P. R.: J. Phys. Chem. **37**, 851 (1933), for references to the literature.

(2) Fajans, K., and Erdey-Gruz, T.: Z. physik. Chem. **A158**, 129 (1931).

(3) Reference 2, p. 106.

(4) Walker, J.: Reference 2, p. 117.

(5) King, J. F., and Romer, A.: J. Phys. Chem. **37**, 663 (1933).

(6) Wyckoff, R. W. G.: The Structure of Crystals, 2nd ed., p. 192. The Chemical Catalog Co., New York (1931).

(7) Fajans, K.: Radioelements and Isotopes, chap. 5. McGraw-Hill Book Co., New York (1931).

THE COLORS OF THE COPPER SALTS

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INTRODUCTION

In 1892 Ostwald (1) pointed out that according to the electrolytic dissociation theory the absorption spectrum of a dilute salt solution must depend exclusively on the absorption spectrum of the solvent, the cation, and the anion. From this it follows that we shall have identical absorption spectra for dilute solutions of different salts with the same colored ion. In accordance with this, dilute solutions of copper sulfate, nitrate, chloride, and bromide should have the same blue color, and it is an experimental fact that they do. The undissociated salt may have a different color and Ostwald called attention to the fact that anhydrous cupric chloride is yellowish-brown, cupric bromide blackish-violet and cupric sulfate gray. Since nobody was especially interested in those days in hydrated ions, the behavior of the copper salts was taken to mean that the copper ion is blue. We see now that that is not necessarily true. All that the experiments really show is that the copper ion common to, and occurring in, those dilute solutions is blue.

Nobody paid any attention at that time to the earlier observation by Vogel (2) that "copper sulphate is one of the few substances which shows the same absorption spectrum in the solid state and in solution. It absorbs the red very strongly up to wave length 620; from there on the absorption decreases rapidly and ends in the yellow-green. Green, bright blue, and dark blue are practically not absorbed, but there is some absorption in the violet."

Since 1908 Hantzsch (3) has taken the ground that there is no necessary relation between color and ionization. He states that colored substances are those which contain an element or group capable of forming a complex of the Werner type. If the complex is saturated completely, all the coördination places being filled, then the color is constant, regardless of the conditions surrounding the complex. Dissociation, salt formation, solution, change of temperature or of solvent, will have no effect on the color. Conversely, if a given color persists through the changing of such conditions, we may regard the saturated complex as persisting through the changes. For those complex states which may not be entirely saturated but become so through a change in conditions, we shall expect an accompanying change in color. If, by any dehydration or substitution, the complex is altered, this will also result in a change of color. Anhydrous salts, which are unsaturated but which become saturated by the addition of water or ammonia molecules or other groups, will change color until complete saturation is reached. After this point there will be no further change in color. If a saturated complex cannot be isolated as a solid or is stable only in presence of a large excess of the solvent, there may be intermediate complexes which will explain the color of certain solutions.

From a study of the chloroplatinate salts of the alkalies, Hantzsch concluded that neither change of dissociation nor change of temperature had any effect on the color. Change of solvent had only a slight effect. An investigation of chromate solutions (4) showed that the acid and its potassium salt had identical absorption, which was independent of dilution and of temperature change. Addition of sulfuric acid up to 10 normal had only a slight effect, accounted for by the formation of some $H_2Cr_3O_{10}$. Solutions of chromic acid in water, alkalies, and methyl alcohol were optically identical in all dilutions examined, except in the water solutions where the slight variation was accounted for by some dichromate ion. The dichromate and chromate solutions were of course unlike. Hantzsch states that the color group of the acid solution is the complex Cr_2O_7, and of the chromate solution CrO_4, irrespective of whether these groups are joined to hydrogen or to an alkali metal. The degree of electrolytic dissociation has no effect on the color because the color of the ion is the same as that of the undissociated complex.

Hantzsch points out that, years before, Sabatier (5) had found that ' the absorption exercised by potassium dichromate dissolved or solid is practically the same as that produced by the chromic acid in the salt."

In a study of alkali permanganates Hantzsch and Clark (6) confirmed these assumptions. Change of temperature or of alkali metal had no effect and the effect of adding sulfuric acid was but small. There was no effect due to change of concentration and the slight effect produced by change of solvent was due to a partial reduction of the permanganates. Hantzsch found that the absorption of solid copper sulfate pentahydrate was very similar to that of its aqueous solution, thus confirming to that extent the earlier observation by Vogel. Hantzsch concluded that the color of both ions is due to the complex, $Cu \cdot 4H_2O$. He believed that this group is also present in dilute solutions of cupric chloride, while the green concentrated solutions contain the unsaturated complex, $Cu \cdot 2H_2O$, which is also present in the solid hydrated salt.

Hantzsch ascribes the intense blue color of the copper ammines to the saturated complex, $Cu \cdot 4NH_3$. Investigation of the copper ammines by Hantzsch and Robertson (7) showed the color to be independent of the anions. The same was true for pyridine solutions, but the complex is apparently less stable in the pyridine solutions, as more is required to produce the blue color. Hantzsch suggests the presence of such groups as $Cu\cdot 3Py\cdot H_2O$ or $Cu\cdot 2Py\cdot 2H_2O$, as being likely. In the case of both solid and solution the saturated complex is the chromophoric group, such as $Cu\cdot 4H_2O$ or $Cu\cdot 4NH_3$. This chromophoric group determines the color regardless of the degree of electrolytic dissociation of the compound in which it appears.

Some of Hantzsch's conclusions had been reached independently and somewhat earlier by Bjerrum (8). "I will next emphasize that it is permissible to assume that the ions of an electrolyte have the same color whether in the free or the bound state, so long as no new complex is formed. This assumption was put forward by me as probable in the spring of 1907 (9). I came to this conclusion by combining the optical data now being presented with the newer views on the constitution of inorganic salts. In the fall of 1907 Hantzsch formulated the same generalization and confirmed it by new experimental data. Just recently some studies on the color of the chromic salts has given me a very good confirmation of this law. I propose to discuss these investigations more fully elsewhere and I will only mention the following here. All normal hexaquochromic salts have exactly the same color, the color of the hexaquochromic ion, even at concentrations at which the salts are only very slightly dissociated into ions."

A possible explanation of the practical identity of color of crystallized copper sulfate pentahydrate and of copper sulfate solutions is given by the theory of complete dissociation. If copper sulfate is 100 per cent ionized under all conditions, there is no reason for any change in color with changing concentration. The difficulty with this is that the monohydrate, $CuSO_4\cdot H_2O$, is green and the anhydrous copper sulfate is colorless. From this it follows that either anhydrous copper sulfate is not dissociated at all or that the copper ion is not blue.

Roscoe and Schorlemmer (10) state that when copper sulfate pentahydrate or trihydrate is heated for some time to 100°C., the monohydrate, $CuSO_4\cdot H_2O$, remains as a bluish-white powder. This is not correct. It was known at least a century ago that monohydrated copper sulfate is green. Graham (11) says that "the sulphate of copper with one atom [molecule] of water was also obtained in a crystallized state by Dr. Thomson and called by him green sulphate of copper." Müller (12) found that the monohydrate is greenish, and we have confirmed his results. Müller looks upon the green color of the monohydrate and the lack of color of the anhydrous sulfate as quite inexplicable.

SPECIAL ASSUMPTIONS

We adopt the general theory of Hantzsch; but the facts now at our disposal make necessary some minor changes in the wording. For instance, the experiments of Dewar (13) show that apparently all colored substances become paler with falling temperature. "The optical properties of bodies cooled to the temperature of boiling liquid air will require long and patient investigation. An interesting fact, easily observed, is the marked change in colour of various bodies. Thus, for instance, oxide, sulphide, iodide of mercury, bichromate of potash, all become yellow or orange; while nitrate of uranium and the double chloride of platinum and ammonium become white. Chromic acid, dilute solutions of iodine in alcohol, strong solutions of ferric chloride and other coloured solutions become greatly changed. Such facts are sufficient to prove that the specific absorption of many substances undergoes great changes at the temperature of −190°C."

When the change with falling temperature involves an apparent change from yellow to white, as is the case with heated zinc oxide, this could easily be considered as contradicting the wording of Hantzsch's theory even though it does not violate the real principle, because the change is only or chiefly one of intensity. In the discussion of the colors of the cupric salts, so far as affected by water and ammonia, we make the following assumptions: —

1. The color of the chromophoric group does not vary appreciably with varying degree of ionization.
2. The color of the chromophoric group becomes paler with falling temperature.
3. The anhydrous cupric ion is not blue. It is probably colorless; but the possibility of its being red is not yet excluded.
4. Cupric copper with one or two molecules of water attached is green.
5. Cupric copper with three or more molecules of water attached is blue.
6. The NH_3 group has an effect similar to that of a water molecule in the copper complex, though the actual blue is different.
7. Copper oxide is blue and not black.
8. Some double salts have an effect which cannot be predicted at present, anhydrous potassium copper sulfate being blue.

GREEN AND BLUE SALTS

Anhydrous cupric sulfate, fluoride, selenate, and perrhenate are colorless. Anhydrous cupric nitrate has been reported by Ditte (14) as nearly colorless, though with a slight greenish tint. It is probable that this discoloration is due to incomplete drying or to slight decomposition, and that the pure anhydrous nitrate is colorless like the other salts cited. If these salts are ionized appreciably, then the anhydrous cupric ion is colorless. If the salts are not ionized appreciably, cupric copper in this form is colorless. We thought, at first, that Hantzsch's theory required that anhydrous cupric ion should be colorless, but there are some anhydrous copper double salts which are red. It would follow equally well from this that anhydrous cupric ion is red. Until we know whether the red or the colorless salts contain the simple cupric group, the question of the color of the anhydrous cupric ion must remain undecided. We shall discuss the question more in detail when considering the brown and red salts. The important thing from our point of view is that the blue ion in hydrated copper sulfate and nitrate cannot be the anhydrous cupric ion.

TABLE 1

Green salts

$CuSO_4 \cdot H_2O$
$CuSO_4\ 2NH_3$
$CuSO_4\ NH_2OH$
$CuSeO_4\ 2NH_3$
$CuSeO_3\ NH_3$
$CuSeO_3 \cdot NH_3 \cdot H_2O$
$CuWO_4\ 2H_2O$
$CuCl_2\ 2H_2O$
$CuCl_2\ 2NH_3$
$CuBr_2\ 2NH_3$
$CuI_2\ 2NH_3$
$CuC_2O_4\ NH_3$
$Cu(CH_3CO_2)_2 \cdot NH_3$
$Cu(CH_3CO_2)_2 \cdot C_6H_5N$
$Cu(CCl_3CO_2)_2\ 2H_2O$
$CuCl_2\ 2KCl \cdot 2H_2O$
$CuBr_2\ 2NH_4Br \cdot 2H_2O$

TABLE 2

Blue salts

$CuSO_4\ 3H_2O$
$CuSO_4\ 5H_2O$
$CuSO_4\ 4NH_3$
$CuSO_4\ 5NH_3$
$CuSO_4\ 4NH_3\ H_2O$
$CuSO_4\ 5NH_2OH$
$CuSeO_4\ 3H_2O$
$CuSeO_4\ 5H_2O$
$CuSeO_4\ 5NH_3$
$CuSeO_3\ 3NH_3$
$CuSeO_3\ 2NH_3\ H_2O$
$Cu(ReO_4)_2\ 4H_2O$
$Cu(ReO_4)_2\ 4NH_3$
$Cu(NO_3)_2 \cdot 3H_2O$
$Cu(NO_3)_2\ 6H_2O$
$Cu(NO_3)_2\ 4NH_3$
$Cu(NO_3)_2\ 6NH_3$
$Cu(NO_2)_2\ 4NH_3$
$CuWO_4\ 4NH_3$
$CuMoO_4\ 2NH_3\ H_2O$
$CuSiF_6\ 6H_2O$
$CuCl_2\ 4NH_3$
$CuCl_2\ 6NH_3$
$Cu(ClO_4)_2\ 4H_2O$
$Cu(ClO_3)_2\ 6H_2O$
$Cu(ClO_3)_2\ 4NH_3$
$Cu(ClO_3)_2\ 6NH_3$
$CuBr_2\ 5NH_3$
$CuBr_2\ 6NH_3$
$Cu(BrO_3)_2\ 4NH_3$
$CuI_2\ 5NH_3$
$CuI_2\ 6NH_3$
$CuI_2\ 4NH_3\ H_2O$
$Cu(IO_3)_2\ 4NH_3$
$Cu(IO_3)_2\ 4NH_3\ H_2O$
$Cu(CNS)_2\ 4NH_3$
$Cu(CNS)_2\ 5NH_3$
$Cu(CNS)_2\ 6NH_3$
$CuSO_4\ M_2SO_4\ 6H_2O$*
$Cu(C_2O_4)\ 5NH_3$
$CuC_2O_4\ 2NH_3\ H_2O$
$Cu(HCO_2)_2\ 4NH_3$
$Cu(HCO_2)_2\ 2C_5H_5N \cdot H_2O$
$Cu(CH_3CO_2)_2 \cdot 4NH_3$
$Cu(CH_3CO_2)_2 \cdot 4C_6H_5N$

* M is K, Rb, Cs, NH_4.

In table 1 is given a list of some cupric salts which are green when crystallizing with one or two molecules of water, ammonia, hydroxylamine, or pyridine. The list is not exhaustive.

The free acids and the sodium salts of the acids in table 1 are colorless, whether hydrated or not, so that there is no reason to believe that the water or ammonia influences the color by being attached to the anion. Where the literature was conflicting as to the color, the salts have been made. Unless the color was perfectly obvious, the crystals were immersed in a liquid of approximately the same index of refraction to eliminate diffuse reflection. The color was then checked by several observers.

In table 2 is given a list of some of the blue cupric salts with three or more molecules of water, ammonia, hydroxylamine, or pyridine.

Chuard (15) claims to have obtained a blue cupric chloride with three molecules of water by working below zero. This would be a welcome confirmation of the theory, but no one else has yet been able to isolate this hydrate. A conspicuous exception to the assumption that cupric salts with three or more molecules of water are blue is $CuCl_2 \cdot CdCl_2 \cdot 4H_2O$, a green salt. We know that cadmium salts in general tend to be hydrated, so that it is probable that part of the water in the crystal is attached to the cadmium, and that the formula should be written $CuCl_2 \cdot 2H_2O \cdot CdCl_2 \cdot 2H_2O$. When the red crystal, $CuCl_2 \cdot LiCl \cdot 2H_2O$, is discussed later, it will be shown that some of the water is undoubtedly attached to the lithium.

BROWN AND RED SALTS

Hantzsch's theory enables us to draw some interesting conclusions in regard to some of the brown and red cupric salts. Anhydrous cupric chloride is a yellow-brown; but Bancroft and Weiser (16) reported that its vapor is violet-red. This has been confirmed by volatilizing the anhydrous chloride rapidly either by itself or in an atmosphere of chlorine to prevent dissociation. In both cases the vapors were distinctly violet-red and condensed to the brown solid. From Hantzsch's theory it follows that the vapor must have a different constitution from the solid. Viard (17) has already shown that cupric chloride and cupric bromide are abnormal, because addition of an excess of concentrated sulfuric acid precipitates anhydrous yellow-brown cupric chloride and anhydrous black cupric bromide, respectively, instead of converting these salts into sulfates. Hantzsch and Carlson (18) state quite definitely that cupric chloride is a pseudo salt.

Qualitatively, solid anhydrous cupric chloride is similar in color to one constituent of a solution of cupric chloride in aqueous hydrochloric acid. Donnan and Bassett (19) showed that the yellow-brown color in these solutions is due to an anion containing copper, $CuCl_3$ or something of that type. Kohlschütter (20) extended the work of Donnan and Bassett, and found that a brown color moved to the anode in concentrated solutions of cupric chloride. In a dilute solution all the copper went to the cathode, but increase of concentration caused some and then more copper to go to the anode. On these facts we conclude that anhydrous cupric chloride is really the copper salt of a chlorocupric acid, and that the formula should be written $Cu(CuCl_4)$ or $Cu(CuCl_3)_2$.

On the other hand, some of the anhydrous double salts are red, such as $CuCl_2 \cdot NH_4Cl$, $CuCl_2 \cdot CsCl$, and $CuCl_2 \cdot KCl$. In these salts we undoubtedly have the cupric chloride having the same chromophoric group as the vapor. It is probable that an x-ray analysis would show a distinct difference between the copper atoms in anhydrous cupric sulfate and those in anhydrous potassium cupric chloride. This is the more plausible because Hendricks and Dickinson (21) have examined some of the hydrated double chlorides and have found evidence indicating a $CuCl_2 \cdot 2H_2O$ group in the ammonium, potassium, and rubidium salts of this type. This confirms our application of Hantzsch's theory. It is a pity that Hendricks and Dickinson did not also study the salt which we write $CuCl_2 \cdot 2H_2O \cdot CdCl_2.2H_2O$.

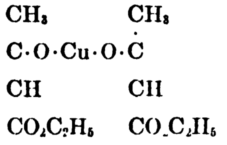
The hydrated double salt of lithium and copper chlorides has the composition, $CuCl_2 \cdot LiCl \cdot 2H_2O$, and is red. Consequently the water must be attached to the lithium chloride and not to the cupric chloride. This is additional evidence for the formula which we have given for hydrated copper cadmium chloride and should be confirmed by an x-ray study.

Engel (22) and Sabatier (23) have made a red compound of cupric chloride, hydrogen chloride, and water. Engel wrote the formula $CuCl_2 \cdot HCl \cdot 3H_2O$ and considered that the compound was derived from the hypothetical trihydrate of cupric chloride. Sabatier wrote the formula $CuCl_2 \cdot 2HCl \cdot 5H_2O$ and did not care how it came to pass. Since neither man had a method of analysis that was worth anything, nobody knows what the composition really was; but the color was red—Sabatier called it a hyacinth red—and changed reversibly from red to green and back again as hydrogen chloride (and water) evaporated off and was put back again.

With the idea of testing Hantzsch's conclusions, anhydrous cupric chloride was added to molten potassium chloride and to molten sodium chloride. In both cases the melt was at once colored red. In time the melt decolorized, presumably owing to volatilization of the cupric chloride. This agrees with what Hantzsch would predict if the cupric chloride vapor is normal, and means apparently that anhydrous cupric ion is red. This contradicts the conclusion drawn from the colorless anhydrous salt. Either copper sulfate, fluoride, selenate, nitrate, and perrhenate form colorless complexes in which copper is not the basic radical, or copper is not the basic radical in cupric chloride vapor. Until some independent evidence is forthcoming, it is impossible to determine which conclusion is right.

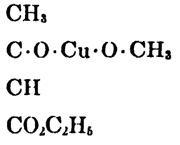
On general principles it seems probable that cupric sulfate and cupric nitrate are normal and not pseudo salts. There is no reason why the vapor of cupric chloride should not be abnormal to some extent. We know that it condenses to a pseudo salt. Sabatier (24) found that cupric bromide is yellowish-red in absolute alcohol and is purple in concentrated solutions of hydrobromic acid, potassium bromide, sodium bromide, lithium bromide, and calcium bromide. There are anhydrous double salts which are red, but apparently no single salts. According to Bödtker (25) anhydrous cupric chloride in absolute alcohol is brown, although the salt which crystallizes is green and has the composition $CuCl_2 \cdot 2CH_3CH_2OH$.

The organic cupric compounds are blue, green, or brown, but apparently never red. Copper acetylacetonate (26) is cobalt-blue when anhydrous and sky-blue when crystallizing with two molecules of water. Copper acetoacetic ethyl ester (27) is green, while the basic methylate is blue. Wislicenus wrote the formulas:



$$\begin{array}{ll} CH_3 & CH_3 \\ C{\cdot}O{\cdot}Cu{\cdot}O{\cdot}C & \\ CH & CH \\ CO_2C_2H_5 & CO_2C_2H_5 \end{array}$$

Copper acetoacetic ester
(green)



$$\begin{array}{l} CH_3 \\ C{\cdot}O{\cdot}Cu{\cdot}O{\cdot}CH_3 \\ CH \\ CO_2C_2H_5 \end{array}$$

Basic methylate
(blue)

The blue form is stable in methyl alcohol and the green form in benzene.

The copper derivative of benzoylcamphor (28) is greenish-yellow in alcohol and greenish-brown in chloroform. Since the red salts occur only under conditions where one would expect pseudo salts, we feel that it is probable that the violet-red of the cupric chloride vapor is abnormal and that the anhydrous cupric ion is colorless.

In fused ammonium acetate at 90°C. cupric chloride, sulfate, nitrate, chlorate, acetate, and oxide are blue, undoubtedly because of the formation of the $Cu(NH_3)_4$ group. In fused ammonium sulfate at 160°C. they are all green, undoubtedly because of the formation of the $Cu(NH_3)_2$ or $Cu(NH_3)$ group. In fused ammonium nitrate at 160°C. all were green except the acetate and oxide, which were blue. All the salts gave a black color in a fused mixture of potassium and sodium nitrates at 300°C. This is apparently due to the formation of undissolved, black, cupric oxide.

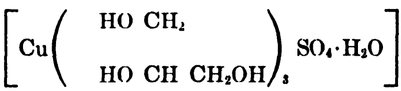
SOLUTIONS

Addition of considerable quantities of sulfuric acid to a copper sulfate solution causes the color to shift from blue to green. This is what should happen if the chromophoric group was being dehydrated.

Gladstone (29) says that "even where different salts of a base have the same colour, the same amount of the base does not give the same intensity of colour. Thus if equal portions of oxide of copper be dissolved respectively in acetic, hydrochloric, nitric, and sulphuric acids, and equally diluted, the acetate will be found to be far deeper in colour than the sulphate, and this again far deeper than the chloride. On being converted into ammoniacal salts, these four approximate more nearly, but are still far from identical in colour."

The acetate did not seem to be entirely trustworthy because of the possible presence of basic salt. Dr. F. H. Getman was kind enough to run spectrophotometric determinations on copper nitrate and copper sulfate solutions. He confirmed Gladstone's observations, finding that solutions of copper nitrate are a deeper blue than the equivalent solutions of copper sulfate. This does not apply of course to very dilute solutions. Since copper nitrate crystallizes with six molecules of water instead of with five, the natural hypothesis is that the copper in undissociated copper nitrate is more highly hydrated than the copper in the corresponding copper sulfate solutions. As yet there is no independent proof of this. We hoped to find in the literature that the solid solutions of copper and zinc sulfates containing seven molecules of water per molecule of salt were much bluer per unit of copper in a given thickness than the corresponding solid solutions with five molecules of water. The literature seems to destroy this hypothesis. Friend (30) says that copper sulfate forms pale blue monoclinic crystals of the series, $CuSO_4 \cdot 7H_2O \cdot ZnSO_4 \cdot 7H_2O$, but dark blue triclinic crystals of the series of solid solutions, $CuSO_4 \cdot 5H_2O \cdot ZnSO_4 \cdot 5H_2O$. This is so inherently improbable that we suspect that proper allowance has not been made for the low copper concentration. This point will be checked as soon as possible.

In the field of non-aqueous solutions the evidence is rather contradictory. Guthrie (31) heated glycerol with cupric sulfate, obtaining an emerald-green solution. This is what one would expect if there were dehydration. Grün and Bockisch (32) say that copper sulfate pentahydrate with dry glycerol gives a dark blue solution. On precipitation with alcohol they obtained a blue oil which could be dried to a blue glass. They write the formula for this:



$$\left[\mathrm{Cu}\left(\begin{matrix}\mathrm{HO\ CH_2}\\ \mathrm{HO\ CH\ CH_2OH}\end{matrix}\right)_3 \mathrm{SO_4 \cdot H_2O}\right]$$

On repeating Guthrie's experiments we got a green solution as he did. We were not using absolutely anhydrous glycerol any more than Guthrie was. It is possible, though not proved, that anhydrous glycerol gives a blue solution and glycerol with small amounts of water gives a green one.

As has been stated, cupric chloride gives a brown solution in absolute alcohol (33) and a green diethylate crystallizes from it. Ley (34) found cupric chloride to be green in alcohol and blue in pyridine. Mason and Mathews (35) reported both green and blue solutions in pyridine just as in water. They suggest that the green is due to cuprous chloride, as this salt is known to be green in pyridine; but this does not yet seem to be necessary. Sammis (36) found that both cupric acetate and cupric formate are blue in pyridine. Mathews and Benger (37) found only two stable solvates of cupric acetate and pyridine, a green one with one molecule of pyridine and a blue one with four molecules. Hantzsch and Robertson (38) state that all the cupric salts give the same blue in dilute solution in aqueous pyridine. They suggest that the blue complex may contain water as well as pyridine.

MISCELLANEOUS CASES

We are still in the descriptive stage with regard to the copper salts. It seems fairly certain that the addition of one or two molecules of water to the copper atom will give a green color, while the addition of three or more will give a blue color; but we do not know why the one is green and the other blue rather than two other colors. Consequently we cannot tell as yet what other grouping will make a copper compound green, blue, or red. The alkaline cupric tartrate solution contains a blue anion, but we could not have predicted that.

Covellite, cupric sulfide, is blue and so apparently is finely divided cupric oxide. In borate and silicate glasses cupric oxide is blue. Here there can be no question of hydrated ions, and the turning green of these glasses when heated too hot is due to the formation of cuprous oxide (39) and has nothing whatsoever to do with the green of such salts as hydrated cupric chloride.

Dioptase, H_2CuSiO_4, is green, and crysocolla, $H_2CuSiO_4 \cdot H_2O$, is blue. Egyptian blue (40) is crystallized $CaO \cdot CuO \cdot 4SiO_2$, and is blue. At 850–900°C. it changes reversibly to a green glass. This is undoubtedly due to the partial decomposition of the cupric salt, but this has not yet been shown analytically. It is possible, though not proved, that dioptase may contain some cuprous salt.

Copper pentammino metachloroantimonate, $Cu(SbCl_6)_2 \cdot 5NH_3$, is blue (41) as it should be, but it becomes green on losing ammonia and that could not have been predicted. The analyses of Scheele's green, Paris green, etc., are so conflicting (42) that one cannot tell anything about them; but copper metarsenite, $Cu(AsO_2)_2$, is said to be colorless and the dihydrated salt, $Cu(AsO_2)_2 \cdot 2H_2O$, is said to be green. That is satisfactory if true.

It is impossible to make any definite statement at present about the basic salts. Basic copper sulfate, $CuSO_4 \cdot 3CuO_2H_2$, is green (43) and $CuSO_4 \cdot CuO$ is said to be orange. Malachite, $CuCO_3 \cdot CuO_2H_2$, is green, and azurite, $2CuCO_3 \cdot CuO_2H_2$, is blue.

The double sulfate of potassium and copper is a very trying case. Cowan and Ferguson (44) say that the dihydrate, $K_2SO_4 \cdot CuSO_4 \cdot 2H_2O$, is bluer than the hexahydrate. The anhydrous salt is blue. One does not like to postulate that potassium sulfate is equivalent to three or more molecules of water in its chromophoric properties and yet Graham (45) put forward what is practically our working hypothesis nearly one hundred years ago. "This double salt [$K_2SO_4 \cdot CuSO_4$] retains its blue color after being fused at a red heat and cooled, and does not become white like the sulphate of copper. Indeed it appears that to be colored, the salts of the oxide of copper require the addition of some other constituent, such as saline water [what is now called water of crystallization], sulphate of potash, or ammonia. Hence if the absolute sulphate of copper could be obtained in a crystallized state [as has since been done], it would be a colorless salt."

A century of progress has brought us back to Graham. Our conclusions and those of Hantzsch would also be acceptable to Gladstone (46). "Every observation made on this salt [cupric chloride] is perfectly explicable on the supposition that the proper color of chloride of copper is brown, and that it forms hydrates which are green or blue, just as the white sulphate of copper becomes blue when hydrated. Some of the facts, too, are *more* easily explained on this view.

"Thus it is hard to imagine that if green be the color of CuCl [$CuCl_2$], and blue that of CuO, HCl [$CuO \cdot 2HCl \cdot H_2O$ or $CuO \cdot 2HCl$], the addition of more HCl should render it green; while it is readily conceivable that the hydrochloric acid should replace a portion of the water in the blue hydrated chloride of copper and form a green double chloride, CuCl, 2HCl [$CuCl_2 \cdot xHCl \cdot yH_2O$].

"If the change of color is to be taken as evidence that crystallized chloride of copper becomes, when treated with a considerable amount of water, CuO, HCl, a parity of reason should lead us to conclude that the bluish-green crystals contain none of the yellowish-brown CuCl [$CuCl_2$]; yet, if we suppose that these crystals actually contain the oxide, we can give no consistent account of the subsequent change of color on solution."

CONCLUSIONS

1. The cupric salts confirm Hantzsch's theory of the identity of color of solid, solution, and vapor when the chromophoric groups are the same in the three states. Conversely, a difference in the color connotes a difference in the chromophoric groups.
2. The color of a chromophoric group is practically independent of the degree of ionization but becomes less intense with falling temperature.
3. Cupric copper with one or two molecules of water is green; with three or more molecules of water it is blue.
4. The ammonia molecule has practically the same effect in a copper complex as has the water molecule, though the shade of the blue is different.
5. Anhydrous cupric sulfate, fluoride, selenate, nitrate, and perrhenate are colorless, which means that the anhydrous cupric ion is colorless if these salts are normal.
6. We have confirmed the statement by Bancroft and Weiser that cupric chloride vapor is red. If the vapor is normal, the theory of Hantzsch requires that the color of the anhydrous cupric ion is red. It is probable that the vapor contains a pseudo salt.

7. Anhydrous cupric chloride is yellow-brown, which is the color of the anion in aqueous hydrochloric acid solutions of cupric chloride and is not the color predicted by the theory of Hantzsch. Consequently anhydrous cupric chloride must contain copper as part of the acid radical. Hantzsch has himself pointed out that anhydrous cupric chloride must be a pseudo salt.

8. The anhydrous double salts, $CuCl_2 \cdot NH_4Cl$, $CuCl_2 \cdot CsCl$, and $CuCl_2 \cdot KCl$, are red, and the chromophoric groups are therefore similar to that in the vapor of cupric chloride.

9. The hydrated double chloride, $CuCl_2 \cdot LiCl \cdot 2H_2O$, is red and must therefore have the two molecules of water attached to the lithium chloride and not to the copper.

10. The hydrated salt, $CuCl_2 \cdot CdCl_2 \cdot 4H_2O$, is green and not blue. Its formula should therefore be written $CuCl_2 \cdot 2H_2O \cdot CdCl_2 \cdot 2H_2O$.

11. By means of x-ray analysis Hendricks and Dickinson have shown the probable existence of the group, $CuCl_2 \cdot 2H_2O$, in some of the green double salts. It is very much to be desired that a systematic study should be made.

12. The anhydrous cupric ion is probably colorless, but may possibly be red.

13. Copper produces a blue color in the borate and silicate glasses and in crystallized Egyptian blue.

14. We do not know why copper is green with one or two molecules of water and blue with three or more molecules of water and consequently we can not predict what other groupings will give blues, greens, or reds.

15. The basic salts are rather hopeless for the present.

16. The anhydrous double sulfate, $K_2SO_4 \cdot CuSO_4$, is blue. It was pointed out by Graham in 1835 that the effect of potassium sulfate is similar to that of water or ammonia.

REFERENCES

(1) OSTWALD: Z. physik Chem. **9**, 579 (1892).

(2) VOGEL: Ber. **11**, 913 (1878).

(3) HANTZSCH: Ber. **41**, 1216, 4328 (1908); Z. physik. Chem. **63**, 367 (1908); **72**, 362 (1910); **84**, 321 (1913); **86**, 624 (1914); Z. anorg. allgem. Chem. **160**, 5 (1927).

(4) HANTZSCH: Z. physik. Chem. **72**, 362 (1910).

(5) SABATIER: Compt. rend. **103**, 49 (1886).

(6) HANTZSCH AND CLARK: Z. physik. Chem. **63**, 367 (1908).

(7) HANTZSCH AND ROBERTSON: Ber. **41**, 4328 (1908).

(8) BJERRUM: Z anorg. Chem. **63**, 146 (1909).

(9) BJERRUM: Kgl. Danske Videnskab. Selskabs Skrifter [7] **4**, 27 (1907).

(10) ROSCOE AND SCHORLEMMER: A Treatise on Chemistry, Vol. 2, p. 451. Macmillan and Co., London (1927).

(11) GRAHAM: Phil. Mag. [3] **6**, 418, (1835).

(12) MÜLLER: Ann. Physik [4] **12**, 777 (1903).

(13) Dewar: Selected Papers of Sir James Dewar, Vol. 1, p. 395. Cambridge University Press, London (1927).
(14) Ditte: Ann. chim. phys. [5] **18**, 320 (1879).
(15) Chuard: Arch. sci. phys. nat. [3] **19**, 477 (1888).
(16) Bancroft and Weiser: J. Phys. Chem. **18**, 328 (1914).
(17) Viard: Compt. rend. **135**, 168 (1902).
(18) Hantzsch and Carlson: Z. anorg. allgem. Chem. **160**, 5 (1927).
(19) Donnan and Bassett: J. Chem. Soc. **81**, 939 (1902).
(20) Kohlschütter: Ber. **37**, 1153 (1904).
(21) Hendricks and Dickinson: J. Am. Chem Soc. **49**, 2149 (1927).
(22) Engel: Compt. rend. **106**, 273 (1888); **107**, 178 (1888).
(23) Sabatier: Compt. rend. **106**, 1724 (1888); **107**, 40 (1888).
(24) Sabatier: Compt. rend. **118**, 430, 1042, 1144, 1260 (1894).
(25) Bödtker: Z. physik. Chem. **22**, 505 (1897).
(26) James: Ann. **226**, 202 (1884)
(27) Wislicenus: Ber. **31**, 3153 (1898).
(28) French and Lowry: Proc. Roy Soc. London **106A**, 489 (1924).
(29) Gladstone: J. Chem. Soc. **8**, 218 (1856).
(30) Friend: A Textbook of Inorganic Chemistry, Vol. 2, p. 282 C. Griffin and Co., London (1924).
(31) Guthrie: Phil. Mag. [5] **6**, 114 (1878).
(32) Grün and Bockisch: Ber. **41**, 3465 (1908).
(33) Bödtker: Z. physik. Chem. **22**, 406 (1897).
(34) Ley: Z. physik Chem. **22**, 77 (1897).
(35) Mason and Mathews: J. Phys. Chem. **29**, 1379, 1507 (1925)
(36) Sammis: J. Phys. Chem **10**, 593 (1906).
(37) Mathews and Benger: J. Phys. Chem. **18**, 264 (1914)
(38) Hantzsch and Robertson: Ber. **41**, 4328 (1908)
(39) Bancroft and Nugent: J Phys. Chem. **33**, 729 (1908).
(40) Laurie: Proc. Roy. Soc London **89A**, 418 (1914).
(41) Weinland and Schmid: Z. anorg. Chem. **34**, 55 (1905).
(42) Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 9, p. 121. Longmans, Green and Co., London (1929).
(43) Roscoe and Schorlemmer: A Treatise on Chemistry, Vol. 2, p. 452. Macmillan and Co., London (1923).
(44) Cowan and Ferguson: J. Chem. Soc. **121**, 1406 (1922).
(45) Graham: Phil. Mag. [3] **6**, 418 (1835).
(46) Gladstone: J. Chem. Soc. **8**, 217 (1856)

THE ACTIVITY COEFFICIENT OF EGG ALBUMIN IN THE PRESENCE OF AMMONIUM SULFATE

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The usual method of determining the activity coefficient of a protein in the presence of salt by measuring its solubility is limited, except in the case of globulins, to comparatively concentrated solutions. Furthermore, necessary information concerning the composition of the solid phase is usually lacking, so that one may actually be dealing with a hydrate whose activity is equal to the product of the activity of the protein by some power of the water activity. It may be pointed out that in the inorganic field solutes are usually treated without regard to hydration even though the solid phase, should it exist, contain water of crystallization. One does not, for example, speak of the activity coefficient of hexahydrated calcium chloride.

PROTEIN ACTIVITIES FROM OSMOTIC EQUILIBRIA

The osmotic pressure of protein, both in the presence and in the absence of other substances, has been recently investigated by a number of workers (1, 2, 3). In the following a method will be developed for determining from such measurements what changes are brought about in the activity coefficient of the unhydrated protein by addition of a third component to the solution. The method is applicable at any temperature between the freezing point of water and that temperature at which the protein coagulates, and may be used throughout the entire solubility range of protein and added crystalloid,—organic or inorganic.

Consider an isoelectric protein solution in equilibrium against water across a membrane impermeable to protein but permeable to all other substances. If successive small amounts of salt or urea be added to the system, there will be reached after each addition a new state of equilibrium. By exerting an appropriate pressure the protein molality may be held constant, leaving as the measured variables the osmotic pressure and the molality of added substance within and outside of the membrane.

Suppose the excess pressure above atmospheric on the protein solution reduced from P to zero. Within the membrane when P is reduced to zero, let us set:

a_1 = activity of water.
a_2 = activity of added substance.
a_3 = activity of protein.
m_2 = molality of added substance.
m_3 = molality of protein.
γ_3 = activity coefficient of protein.
$\bar{V}_1$ = partial molal volume of water.
$\bar{V}_2$ = partial molal volume of added substance.

Let a_1^*, a_2^*, m_2^* represent the corresponding quantities in the protein-free outer solution. The symbols and general method of treatment are those of Lewis and Randall (4). We have the two Duhem equations

$$m_3 \, d \ln a_3 = -55.51 \, d \ln a_1 - m_2 \, d \ln a_2 \tag{1}$$

$$55.51 \, d \ln a_1^* = -m_2^* \, d \ln a_2^* \tag{2}$$

Also

$$RT \ln a_1 = RT \ln a_1^* - \bar{V}_1 P \tag{3}$$

or

$$d \ln a_1 = d \ln a_1^* - \frac{\bar{V}_1}{RT} \, dP \tag{4}$$

Similarly

$$d \ln a_2 = d \ln a_2^* - \frac{\bar{V}_2}{RT} \, dP \tag{5}$$

Substituting equations 4 and 5 in equation 1,

$$m_3 \, d \ln a_3 = \frac{55.51 \bar{V}_1 + m_2 \bar{V}_2}{RT} \, dP - 55.51 \, d \ln a_1^* - m_2 d \ln a_2^* \tag{6}$$

From equations 6 and 2

$$d \ln a_3 = \frac{55.51 \bar{V}_1 + m_2 \bar{V}_2}{m_3 RT} \, dP + \frac{m_2^* - m_2}{m_3} \, d \ln a_2^* \tag{7}$$

Changing to common logarithms and introducing γ_3

$$d \log \gamma_3 + d \log m_3 = \frac{55.51 \bar{V}_1 + m_2 \bar{V}_2}{2.3 \, m_3 RT} \, dP + \frac{m_2^* - m_2}{m_3} \, d \log a_2^* \tag{8}$$

Integrating

$$\int d \log \gamma_3 = \int \frac{55.51 \bar{V}_1 + m_2 \bar{V}_2}{2.3 \, m_3 RT} \, dP + \int \frac{m_2^* - m_2}{m_3} \, d \log a_2^* - \int d \log m_3 \tag{9}$$

This equation enables us to calculate changes in γ_3 from measurements of osmotic pressure and the distribution of added substance between the protein-containing and protein-free compartments of an osmometer. The partial molal volumes may be measured or assumed to be the same as in the protein-free solution. Activities outside are determined by the usual methods.

This calculation has been carried through using the careful data of Sörensen (5) and his coworkers on the osmotic pressure of egg albumin in the presence of ammonium sulfate. Since the activity coefficient of ammonium sulfate is not known, it has been assumed equal to that of sodium sulfate as given by Åkerlof (6). In the calculation of m_3 the molecular weight was taken as 34,500 and the nitrogen factor as 6.45. The value of $55.51\,\bar{V}_1 + m_2\bar{V}_2$ is from table 32, p. 158 of reference 5. In the most dilute salt solution γ_3 is set equal to one.

Table 1 of this paper gives values of m_2^*, m_2, m_3, $\frac{m_2^* - m_2}{m_3}$, $-\log \gamma_2^*$, and $\log a_2^*$ obtained from tables 55, 56, and 57, pp. 334, 335, 336, and 337 of reference 5, and values of γ_2 from reference 6. These are plotted in figure 1 with $\frac{m_2^* - m_2}{m_3}$ as ordinate and $\log a_2^*$ as abscissa. A smooth curve through these points permits a graphical integration of the second term of the right-hand member of equation 9. The first term of the same member contributes little to $\log \gamma_3$ and is easy to evaluate. The quantity

$$\frac{55.51\bar{V}_1 + m_2\bar{V}_2}{2.3\, m_3 RT}$$

is found to be approximately constant, so that one may use an average value over any interval and set

$$\frac{1}{2.3RT}\int_{P_1}^{P_2} \frac{55.51\bar{V}_1 + m_2\bar{V}_2}{m_3}\,\mathrm{d}P = \frac{1}{2.3RT}\int_{P_1}^{P_2} \frac{V}{m_3}\,\mathrm{d}P = 5.3 \times 10^{-3}\,(P_2 - P_1) \quad (10)$$

where P is expressed in centimeters of water and $T = 291$.

In table 2 are given the steps in a graphical integration of equation 9. The solutions are selected from table 55, pp. 334 and 335 of reference 5 in such a manner as to cover the concentration range of ammonium sulfate in approximately equal steps. Values for $\frac{m_2^* - m_2}{m_3}$ are read from figure 1. It may be observed that the osmotic pressure term is negligible. Figure 2 shows that the logarithm of the activity coefficient of egg albumin is a linear function of the ammonium sulfate molality within the membrane. The decrease in the activity coefficient of egg albumin with increasing salt

TABLE 1

EXPERIMENT NO	$m_2^{\#}$	m_2	$m_3 \times 10^3$	$\frac{m_2^{\#} - m_2}{m_3}$	$-\log \gamma_2^{\#}$	$-\log a_2^{\#}$
98	1 836	1 763	3 657	19 96	0 803	1 015
104	1 761	1 693	3 700	18 38	0 794	1 042
62	1 502	1 433	4 074	16 94	0 761	1 150
112	1 407	1 358	3 374	14 52	0 748	1 198
97	1 388	1 335	3 615	14 66	0 745	1 207
103	1 229	1 186	3 550	12 11	0 722	1 294
61	1 207	1 160	3 932	11 95	0 719	1 309
90	1 183	1 137	3 951	11 64	0 715	1 324
87	1 182	1 140	3 850	10 91	0 714	1 321
89	1 181	1 137	3 921	11 22	0 714	1 324
88	1 178	1 131	3 977	11 82	0 714	1 327
163	1 170	1 123	4 038	11 64	0 713	1 333
164	1 168	1 123	3 977	11 32	0 712	1 333
137	1 167	1 118	3 580	13 69	0 712	1 333
110	1 046	1 010	3 338	10 78	0 692	1 417
111	1 042	1 004	3 295	11 53	0 691	1 417
105	0 8470	0 8214	3 375	7 59	0 657	1 585
96	0 6537	0 6362	3 461	5 06	0 619	1 810
146	0 3283	0 3200	3 193	2 60	0 521	2 410
95	0 3191	0 3133	3 336	1 74	0 517	2.437
94	0 1945	0 1930	3 381	0 44	0 446	2 869
93	0 1299	0 1305	3 349	−0 18	0 396	3 244
82	0 0677	0 0686	3 772	−0 24	0 320	3 865
92	0 0642	0 0633	3 186	+0 28	0 315	3 877
81	0 0336	0 0349	3 772	−0 34	0 250	4 570
91	0 0331	0 0347	3 350	−0 48	0 246	4 576
117	1 577	1 518	3 445	17 12	0 772	1 120
114	1 519	1 463	3 396	16 49	0 764	1 144
108	1 412	1 355	3 500	16 29	0 749	1 195
116	1 209	1 161	3 315	14 48	0 719	1 309
113	1 030	0 9960	3 274	10 38	0 690	1 429
115	0 8209	0 7979	3 282	7 01	0 652	1 612
107	0 6812	0 6605	3 194	6 48	0 624	1 771
129	0 3291	0 3216	3 145	2 39	0 522	2 413
122	0 1923	0 1907	3 233	0 50	0 445	2 881
121	0 1298	0 1279	3 140	0 61	0 396	3 247
84	0 0680	0 0679	3 851	0 03	0 322	3 868
120	0 0637	0 0635	3 086	0 06	0 315	3 931
83	0 0331	0 0332	3 802	−0 03	0 246	4 576
119	0 0317	0 0318	3 087	−0 03	0 242	4 621
167	1 531	1 478	3 452	15 35	0 766	1 141
166	1 407	1 352	3 587	15 33	0 748	1 198
127	1 193	1 154	3 333	11 70	0 716	1 315
165	1 081	1 046	3 515	9 96	0 698	1 390
106	1 039	1 009	3 435	8 73	0 691	1 420
168	0 7625	0 7591	3 693	9 20	0 641	1 675
133	0 3312	0 3249	3 092	2 04	0 523	2 407

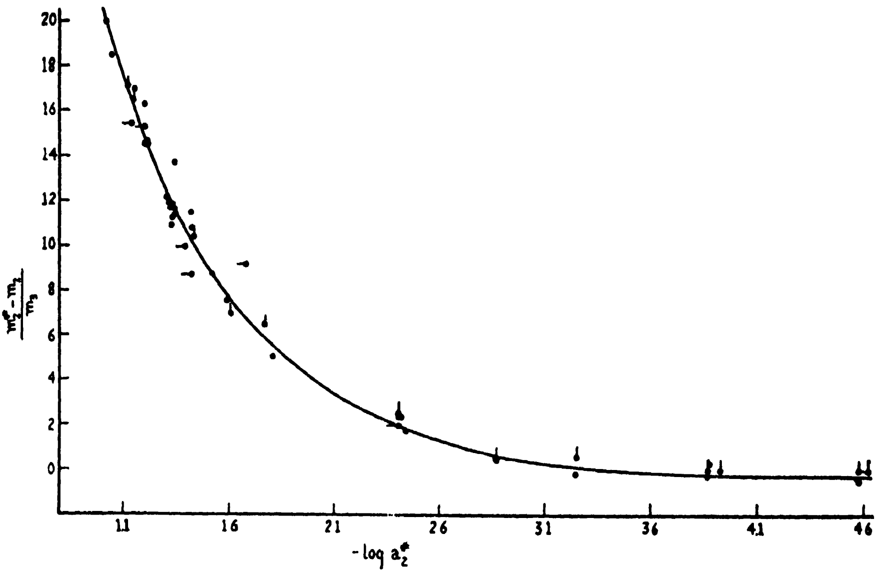

Fig. 1.

| Solutions of pH 4.6; • solutions of pH 4.9; —• solutions of pH 5.3

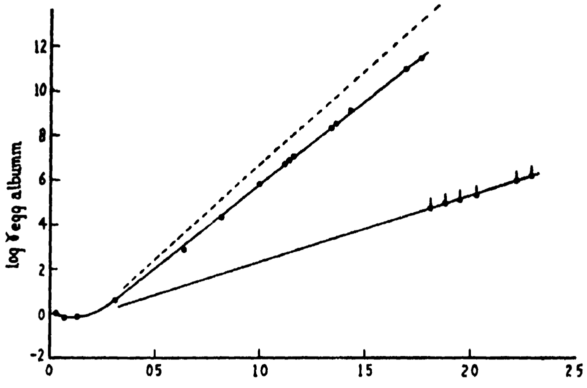

Fig. 2.

• Log activity coefficient egg albumin from osmotic equilibria.

| Log activity coefficient egg albumin from solubilities, assuming log γ = Constant − log m_3.

The broken line shows log activity coefficient egg albumin from solubilities corrected for changing water activity, assuming the solid phase to contain 0.22 g. water per gram of protein. In the case of the two curves from solubilities only the slopes are significant.

concentration at low salt concentrations may be real, as in the case of globulins, or may possibly be an error due to a small amount of ammonia in the egg albumin, which would reverse the sign of $\frac{m_2^* - m_2}{m_3}$. The author is inclined to accept the first interpretation.

TABLE 2

EXPERIMENT NO	m_2	$m_3 \times 10^3$	V	P	$\frac{1}{2\ 3\ RT}\int\frac{V}{m_3}\,\mathrm{d}P$	$\frac{m_2^* - m_2}{m_3}$	$-\log a_2^*$	$\int\frac{m_2^* - m_2}{m_3}\,\mathrm{d}\log a_2^*$	$-\int\mathrm{d}\log m_3$	$\log\gamma_3$
91	0 03	3 35	1003	73 1	0	−0 3	4 576	0	0	0
82	0 07	3 77	1005	79 5	+0 03	−0 2	3 865	−0 18	0 06	−0 21
93	0 13	3 35	1008	75 7	+0 01	+0 1	3 244	−0 18	0	−0 17
95	0 31	3 37	1019	73 7	0	1 8	2 437	+0 59	0 01	+0 58
96	0 64	3 46	1039	73 1	0	5 5	1 810	2 88	0 02	2 86
105	0 82	3 38	1052	67 9	−0 03	7 9	1 585	4 38	0 01	4 34
111	1 00	3 30	1064	62 1	−0 06	10 3	1 417	5 91	0	5 85
137	1 12	3 58	1072	61 7	−0 07	11 7	1 333	6 84	0 03	6 74
90	1 14	3 95	1073	72 3	0	12 0	1 324	6 94	0 08	6 86
61	1 16	3 93	1075	66 8	−0 03	12 2	1 309	7 13	0 07	7 03
97	1 34	3 62	1087	58 2	−0 07	14 6	1 207	8 49	0 03	8 39
112	1 36	3 37	1088	53 0	−0 10	14 8	1 198	8 62	0 01	8 51
62	1 43	4 07	1095	59 3	−0 07	16 0	1 150	9 36	0 09	9 20
104	1 69	3 70	1112	43 9	−0 15	19 2	1 042	11 26	0 05	11 06
98	1 76	3 66	1118	39 6	−0 17	20 0	1 015	11 79	0 04	11 58

TABLE 3

EXPERIMENT NO	m_2	$m_3 \times 10$	$\log m_3 + 5$	$1\ 57 - \log m_3$
1	1 81	59 42	1 77	4 80
2	1 88	40 17	1 60	4 97
3	1 95	26 18	1 42	5 15
4	2 03	14 98	1 18	5 39
5	2 22	3 467	0 54	6 03
6	2 29	2 080	0 32	6 25

PROTEIN ACTIVITIES FROM MEASUREMENTS OF SOLUBILITY

That the solubilities of proteins are affected by salts has long been known. Cohn (7) pointed out that the logarithm of protein solubility is, in the case of egg albumin and of pseudoglobulin, a linear function of salt concentration. This relation has since been found by Florkin (8) to hold for fibrinogen, and by Green (9) for hemoglobin. It is sometimes assumed that

$$\log \gamma_{\text{protein}} = \text{Constant} - \log \text{Solubility}_{\text{protein}} \tag{11}$$

and a calculation made in accordance with the above from table 39, p. 221 of reference 5 is shown in table 3 and plotted in figure 2.

One may see that a great discrepancy exists between the slope of the straight line through these points and the values of log γ_3 obtained by the previous method. If the solid phase contains water as water of crystallization and we choose unhydrated protein as one component, however, equation 11 cannot hold. The reaction is not

$$\text{Protein (dissolved)} \rightleftharpoons \text{Protein (solid)} \tag{12}$$

but

$$\text{Protein (dissolved)} + n\text{H}_2\text{O} \rightleftharpoons \text{Protein hydrate (solid)} \tag{13}$$

so that if a_1 = activity of water,
m_2 = molality of ammonium sulfate,
a_3 = activity of protein,
m_3 = solubility of protein,
γ_3 = activity coefficient of protein,
a_4 = activity of protein hydrate, and
n = moles of water per mole of protein in the hydrate,

$$a_1^n \ a \ = a_4 = \text{Constant} \tag{14}$$

therefore

$$n \,\mathrm{d} \log a_1 + \mathrm{d} \log \gamma_3 + \mathrm{d} \log m_3 = 0 \tag{15}$$

and

$$\frac{\partial \log \gamma_3}{\partial m_2} \qquad \frac{\partial \log m_3}{\partial m_2} \qquad n\frac{\partial \log a_1}{\partial m_2} \tag{16}$$

but

$$\frac{\partial \log a_1}{\partial m_2} = \frac{\partial \log a_1}{\partial \theta} \frac{\partial \theta}{\partial m_2} \tag{17}$$

where θ is the freezing point depression.

$$\frac{\partial \log a_1}{\partial \theta} = -0\ 00421 \tag{18}$$

(See reference 4, p. 284.) Also for ammonium sulfate (reference 10), when m_2 is about 2,

$$\frac{\theta}{m_2} = 3\ 21 \tag{19}$$

We shall set $\frac{\partial\theta}{\partial m_2}$ equal to this, and neglect the effect of protein on a_1. Solid egg albumin hydrate contains 0.22 g. of water per gram of protein (reference 5, p. 210).

$$n = \frac{34{,}500 \times 0.22}{18} = 422 \tag{20}$$

From table 3

$$-\frac{\partial \log m_3}{\partial m_2} = 3.0 \tag{21}$$

Thus

$$\frac{\partial \log \gamma_3}{\partial m_2} = 3.0 + 422 \times 0.00421 \times 3.21 = 8.7 \tag{22}$$

which agrees satisfactorily with the slope 7.6 obtainable from table 2 when one considers all the assumptions made in getting constants necessary for the computation, and the fact that in one case the protein concentration is held constant while in the other it varies greatly.

SUMMARY

The logarithm of the activity coefficient of egg albumin in the presence of ammonium sulfate has been calculated from osmotic data and found to be a linear function of the salt concentration. These activity coefficients are in satisfactory agreement with solubility measurements when account is taken of the composition of the solid phase.

REFERENCES

(1) Adair, G. S.: Proc. Roy. Soc. London **A120,** 573 (1928); **A126,** 16 (1929); J. Am. Chem. Soc. **51,** 696 (1929).
(2) Burk, N. F., and Greenberg, D. M.: J. Biol. Chem. **87,** 197 (1930).
(3) Burk, N. F.: J. Biol. Chem. **98,** 353 (1932).
(4) Lewis, G. N., and Randall, M.: Thermodynamics and the Free Energy of Chemical Substances. McGraw-Hill Book Co., New York and London (1923).
(5) Sörensen, S. P. L.: Compt. rend. trav. Lab. Carlsberg **12** (1917).
(6) Åkerlöf, G.: J. Am. Chem. Soc. **48,** 1160 (1926).
(7) Cohn, E. J.: Physiol. Rev. **5,** 349 (1925).
(8) Florkin, M.: J. Biol. Chem. **87,** 629 (1930).
(9) Green, A. A.: J. Biol. Chem. **93,** 495 (1931).
(10) International Critical Tables, Vol. IV, p. 255. McGraw-Hill Book Co., New York (1928).

NEW BOOKS

Réel et Déterminisme dans la Physique Quantique. By E. **Meyerson**, with a preface by L. de Broglie. 50 pp. Monograph No. 68 of the scientific and industrial series published by Hermann & Co., Paris, 1933.

This volume is the first of a group of monographs published under the direction of Professor L. de Broglie on the philosophy of the sciences. These philosophical treatises are to be part of the large scientific series mentioned. In the present essay the concepts of physical science are discussed in the light of quantum theory. References are given to the author's own works and to seven original articles. No headings, no subdivisions, no index, and the discursive style make the volume very slow reading when one considers the difficult subject matter dealt with.

George Glockler.

Wege zur physikalischen Erkenntnis. Reden und Vorträge. By **Max Planck**. 22.5 x 15 cm.; ix + 280 pp. Leipzig: S. Hirzel, 1933. Price: bound, 8 marks; unbound, 6 marks.

Professor Planck has collected in this volume eleven lectures, given over a period from 1908 to 1933, in which the central theme is the physical conception of the universe and its reactions on philosophy. The physicist's picture of the universe has changed during this period very considerably, and in recent times it has seemed to some that all hope of retaining the law of causality, and of going beyond the purely formal descriptions of events by mathematical methods, would have to be abandoned. Professor Planck, whose own work has been most concerned in this change of outlook in physics, does not adopt this rather pessimistic view, and in this series of lectures he has examined the consequences of each new step in the physical description of events. The lectures are, in fact, the result of careful thought on the part of a scientist who has always tried to see beyond the narrow walls of the physical laboratory, and the volume is one in which former students of the great physicist will recognize his inimitable command of his subject and the great power of exposition and logical clarity which characterize all his work. The Nobel Lecture on the quantum theory is included. The volume is one of considerable interest and value.

J. R. Partington.

The Cotton Effect. By S. **Mitchell**. 22 x 13.5 cm.; vii + 92 pp. London: G. Bell and Sons, 1933. Price: 7 s. 6 d.

The opening chapter of this excellent little book is devoted to a consideration of the fundamental conceptions of refractive dispersion, normal and anomalous dispersion, double refraction, plane, circular, and elliptical polarization, circular double refraction, anomalous rotatory dispersion, the detection of elliptical vibration, the Cotton effect, and circular dichroism. These terms and the causes of the various phenomena are fully explained, together with an account of the history of the work which led to their recognition. This is followed by a description of the measurement of absorption spectra. The Hartley method and its modifications are described, as also are the uses of the spectrophotometer and the polarization-photometer. The third chapter is devoted to theoretical considerations and in this the equations of Sellmeier and Drude, connecting refractive dispersion and absorption, are considered together with the modern developments of Kuhn. The measurement of rotation and ellipticity with modern instruments constitutes the subject of the fourth chapter. The work of Tschugaev, Lowry and others on rotatory dispersion and circular dichroism in connection with a number of organic and inorganic substances is dealt with in the next chapter, whilst the final chapter deals with asymmetrical photochemical action. Here many unsuccessful attempts at asymmetric synthesis are described, together with the technique of the author which led to successful results.

The book presents an excellent summary of the present knowledge of the subject and it can be recommended with confidence.

JAMES F. SPENCER.

The Conductivity of Solutions. By C. W. DAVIES. 2nd edition. 21.5 x 14 cm.; x + 281 pp. London: Chapman and Hall, 1933. Price: 15 s.

Since the first edition of this book was reviewed in The Journal of Physical Chemistry in 1930, it is only necessary to say that the size has been increased by about eighty pages by the inclusion of new material, two extra chapters on the practical applications of conductivity measurements having been added, and several of the sections in the earlier text have been brought up to date by the inclusion of recent work. A brief account of Wien's experimental method and the results, further investigations on non-aqueous solutions, the dissociation of weak ternary electrolytes, the recent investigations on the viscosity of electrolytes, and a very brief mention of the theory of Gronwall, La Mer, and Sandved are the principal additions. The accounts of the theories are very sketchy and the mathematical side of the subject is neglected. On the other hand, the numerical applications of the equations, which are assumed, are good, and there are useful tables of data.

J. R. PARTINGTON.

Theoretical Physics. Vol. I. Mechanics and Heat (Newton-Carnot). By W. WILSON. 325 pp.; 80 diagrams. New York: E. P. Dutton & Co., 1932.

The author covers the usual field of mathematical physics. Chapters I and II cover an introduction to vector and tensor analysis, the theorem of Gauss, Green and Stokes and Fourier's expansion. Dynamics, wave propagation, elasticity, hydrodynamics, and viscous fluids are dealt with in chapters III to IX. The kinetic theory of gases and statistical mechanics take up chapters X and XI and the first and second laws of thermodynamics with applications conclude the volume in chapters XII to XIV. The book is written in mathematical language, of course, and the explanatory paragraphs written in ordinary language are short, concise, and reduced to the minimum. Because he uses the concise expressions of mathematics, the author can cover the tremendous fields of human thought outlined above and do it well in the allotted space. The student who wishes to read further about the subject matter will welcome the bibliography added at the end of each chapter. This volume is the first one of three on the subject of theoretical physics, the second and third volumes are to cover electromagnetism, optics and relativity, quantum dynamics respectively. The first volume is an excellent treatise on the topics covered and the other volumes of the set will be awaited with great interest.

GEORGE GLOCKLER.

Lehrbuch der physikalischen Chemie. By KARL JELLINCK. Band IV, Lieferung 3. 25 x 16.5 cm.; xiv + 625-890 pp. Stuttgart: F. Enke, 1933. Price: 26 marks.

The present issue completes the fourth volume of the work, and a fifth volume is to appear. The subject dealt with is the phase rule, and the treatment is intended to be representative rather than exhaustive. One- and two-component systems are treated by means of representative examples, a good feature being the inclusion of uncondensed systems in some detail, since this subject, being perhaps rather more difficult, tends to be neglected. Quantitative work is introduced when available, and the diagrams are plentiful and well drawn. In the treatment of three-component systems with one liquid and one or more solid phases, the Schreinemaker isothermal method is generally used, but a few examples of the van't Hoff method are also given. There is a section on thermal analysis as applied to three-component systems, and the usual detailed discussion of double salts with and without transition points. Mixed crystallization in three-component systems, and uncondensed ternary systems are dealt with only briefly, but references to literature are given fully throughout. Four-component systems are represented by reciprocal salt pairs, and by a system composed of water and three salts with a common ion. No higher systems are treated. The book provides a compact and clear account of a large subject, and maintains the high standard of previous volumes. It is a work of great merit and should be available to all physical chemists

J. R. Partington.

Essai sur la Chimie Comparée. Les Corps Simples. By Ionel N. Longinescu. 25 x 16 cm.; vii + 98 pp. Paris: Les Presses Universitaires de France, 1932. Price: 30 francs.

The opinion of the author of this essay is that the comparative method is the one best suited both to the progress of and to the learning of a science. As in the case of comparative anatomy the animal may be constructed by the aid of a single organ, so from knowledge of a single property of a substance, all others might be derived, or the relations traced from family to family.

An electrochemical, thermochemical, photochemical, and analytical classification of the chemical elements is considered, but the basis actually adopted is a modification of the Mendeléeff periodic system. There is thus very little that is novel in the presentation, with a tendency rather to emphasize similarity and to ignore differences.

The author states that he may, at a later date, deal with binary substances; if he does, it will be interesting to see how these will fare under the comparative method.

W. H. Patterson.

Fortschritte der Serologie. By Hans Schmidt. Vol. XXX of "Wissenschaftliche Forschungberichte." 22 x 15 cm.; xi + 191 pp. Dresden and Leipzig: Theodor Steinkopff, 1933. Price: bound, 13.20 RM; unbound, 12.00 RM.

The series of "Wissenschaftliche Forschungsberichte," of which the present work is a number, undertakes to sift the chaff from the wheat and so differs from the somewhat distressing compilations with which we are familiar in German literature. The present volume consists of a survey of the present state of serology, using this term in the strict sense as applying to phenomena observed in the test tube. All reference to immunity and anaphylaxis is excluded, these being dealt with in another volume. It is not to be supposed that a specialist in serological reactions will find this review of much use to him, but the worker in allied subjects will welcome it as a survey of a field which is possibly overloaded with minutiae. The author, in order to produce anything but a trivial account in less than two hundred pages, has naturally been forced to pick and choose. Some subjects are frankly referred to recent reviews after a mere introductory outline, but those which are of considerable topical interest, such as the chemical nature of antigens and their bearing upon agglutination, are dealt with critically and fully from the point of view of presenting a broad outline, though not of course in the matter of detail. For those who may require it, two sources of further information are provided, namely, references to the authors cited, which indicate a special regard for the work of British and American workers, and references to more extensive reviews in different languages.

P. FILDES.

James Clerk Maxwell. 146 pp. New York: The Macmillan Co. Price: $2.50.

This is a commemoration volume containing essays by J. J. Thomson, Planck, Einstein, Larmor, Jeans, Garnett, Fleming, Lodge, Glazebrook, and Lamb.

It is apparent that those who through direct personal acquaintance or who through closely allied intellectual achievement could speak authoritatively were called upon to participate directly in the centenary of Maxwell's birth and it is inevitable that those whose intellectual interests lie in the fields of physics, chemistry, and mathematics will greatly appreciate the evaluations given in these essays. The laity however will appreciate the volume only in part because of the profoundly technical character of Maxwell's work.

The volume has an additional interest in that it gives the reader the reactions of master minds at a time when new concepts are in the foreground.

HENRY A. ERIKSON.

Gmelin's Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Number 35: Aluminium. Teil B, Lieferung 1: Die Verbindungen des Aluminiums. 25.5 x 17.5 cm.; ix + 308 pp. Berlin: Verlag Chemie, 1933. Price: 48 marks. Subscription price: 42 marks.

The present volume deals with the oxides, oxide hydrates, nitride, halogenides, sulfate, and several less important compounds. The technical processes are fully dealt with, including aluminum chloride for oil cracking, and recent literature and patents are very fully covered. The recent papers of Weiser and Milligan, and of Edwards and Tosterud, in This Journal came too late for inclusion in the literature on the oxide hydrates, but the book by Edwards, Frary, and Jeffries on the aluminum industry is frequently cited and the technical information is complete and up-to-date. The volume is an indispensable addition to the literature of chemistry.

J. R. PARTINGTON.

L'Univers en Expansion. By HENRI MINEUR. Actualités Scientifiques et Industrielles, No. 63. Publiés sous la direction de M. L. de Broglie. Paris: Hermann & Cie, 1933.

The present volume is No. 63 in the series of monographs on scientific subjects, chiefly those in theoretical physics, published under the direction of de Broglie. It gives one of the very few up-to-date discussions of the subject, which is not merely intended for the layman or the general public, but treats the entire problem concisely, "from the ground up," using directly the equations of Einstein, de Sitter, Lemaître, and others, and discusses the properties of the various types of space resulting from each. It closes with a résumé of Eddington's calculations of the cosmological constant λ. It is clearly written, and gives an admirable summary of this *question brulante* of the present, and may be heartily recommended to any one interested in the problem.

W. J. LUYTEN.

THE SOLUBILITY OF ACETYL-*O*-TOLUIDINE IN VARIOUS SOLVENTS[1]

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INTRODUCTION

In previous communications to This Journal, Collett and Lazzell have reported a series of measurements of solubility for several systems of disubstituted benzene derivatives, namely the nitroanilines (1), the aminobenzoic acids (2), the nitrobenzoic acids (3), and the dihydroxybenzenes (4).

A survey of the literature revealed that no systematic investigation of the solubility of the acetyltoluidines in a series of solvents had ever been reported. The present investigation was undertaken with the primary object of obtaining data for another system of disubstituted benzene derivatives which could be used in the study of the solubility relations of systems of this type. These measurements are of value in themselves, since the acetyltoluidines are of some commercial importance.

In this paper are presented solubility measurements for acetyl-*o*-toluidine in methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, chloroform, carbon tetrachloride, benzene, diethyl ether, and water from about 25°C. to 110.3°C., the melting point of the solute. The heat of fusion of acetyl-*o*-toluidine has been calculated.

MATERIALS

A. Acetyl-o-toluidine

The acetyl-*o*-toluidine used in these determinations was the best grade obtainable from the Eastman Kodak Company. As received, it had a melting point of 107.1°C. After one crystallization from water it melted at 110.3°C. A little tar was observed to be formed around the beaker. A second crystallization from water gave no tar and no further change in melting point. Recrystallization of this product from alcohol gave no further change in melting point. For this reason it was concluded that the material which had been crystallized from water once and thoroughly dried was of sufficient purity for use. The melting point given in the International Critical Tables is 110.3°C. Before using, the material was dried over calcium chloride and then over concentrated sulfuric acid.

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[1] Contribution No. 92 from the Department of Chemistry, Division of Industrial Sciences of West Virginia University.

[2] From a part of the thesis presented to the Graduate School of West Virginia University, in June 1932, by James Lester Hall in candidacy for the degree of Master of Science.

B. Solvents

All the solvents used in this investigation, except water, were carefully dried and distilled several times until a product having a satisfactory boiling range was obtained. Freshly redistilled water was used. In table 1 are listed the boiling ranges and the refractive indices of the solvents used. All temperatures were obtained by use of thermometers certified by the Bureau of Standards and corrections were made in each case for stem emergence. The boiling ranges were all reduced to 760 mm. pressure.

TABLE 1

Physical properties of solvents

SOLVENT	BOILING RANGE	BOILING POINT (INTERNATIONAL CRITICAL TABLES)	REFRACTIVE INDEX	
			Found	International Critical Tables
	degrees C	*degrees C*		
Methyl alcohol ..	64.3	64.5	1.3291	1.329
Ethyl alcohol	78.4	78.5	1.3618	1.361
n-Propyl alcohol	97.1	97.8	1.3854	1.386
Isopropyl alcohol	82.0–82.2	82.3	1.3790	1.378
n-Butyl alcohol	117.9	117.7	1.3992	1.3993
Isobutyl alcohol	106.9 107.0	107.3	1.3958	1.396
Benzene	79.98–80.02*	79.6	1.5012	1.5014
Acetone.	55.8–56.0	56.1	1.3599	1.3591
Carbon tetrachloride	76.5	76.8	1.4603	1.4607
Chloroform	60.8–61.1	61.2	1.4461	1.4467
Diethyl ether	34.25–34.35	34.5	1.3528	1.3526

* Richards and Barry (J. Am. Chem. Soc. **37**, 996 (1915)) give 80.2°C. as the boiling point of benzene.

METHOD

The experimental data on solubility presented in this article were obtained by the synthetic method. Details of the procedure used here are fully explained in a previous paper (5).

All of the determinations were checked by at least two trials and many were repeated by duplicate bulbs.

TABLE 2

Experimental values of the solubility of acetyl-o-toluidine in terms of mole percentage

c	t	c	t	c	t
Methyl alcohol		Ethyl alcohol		*n*-Propyl alcohol	
	degrees C		*degrees C*		*degrees C*
100.00	110.3	100.00	110.3	100.00	110.3
86.00	102.4	85.50	102.0	86.80	103.2
83.60	100.7	79.95	99.2	63.30	87.4
74.35	94.9	71.90	93.5	53.20	79.2
69.50	91.0	64.60	87.7	49.38	76.2
63.60	86.5	54.94	80.8	40.40	68.9
59.80	83.3	47.55	75.2	32.30	60.0
55.48	79.6	41.37	69.9	20.15	45.0
45.55	71.0	31.80	60.3	15.18	36.7
36.45	61.4	24.45	52.3		
26.50	47.9	13.99	34.8		
22.34	42.1	9.20	23.9		
10.31	18.3				
Isopropyl alcohol		*n*-Butyl alcohol		Isobutyl alcohol	
100.00	110.3	100.00	110.3	100.00	110.3
92.80	106.2	88.20	103.5	87.60	103.1
82.20	100.2	67.80	90.6	78.80	98.0
72.50	94.4	63.10	86.7	67.92	91.4
61.10	86.7	50.35	77.2	57.90	83.0
51.70	79.8	42.14	70.8	50.06	77.2
41.30	71.8	33.40	62.1	42.35	72.3
33.94	66.0	21.58	47.7	30.51	60.7
25.61	57.1	10.50	26.5	20.74	49.2
23.13	54.1			10.30	30.1
21.72	52.2				
11.31	34.5				
Benzene		Acetone		Carbon tetrachloride	
100.00	110.3	100.00	110.3	100.00	110.3
87.82	103.6	91.60	105.5	91.24	105.7
80.30	98.6	82.52	100.3	77.75	98.1
69.48	92.6	71.30	93.4	66.73	91.9
60.30	87.2	68.50	91.6	59.63	88.0
44.54	76.8	52.82	79.9	49.44	81.8
35.97	71.5	38.37	68.1	38.06	75.4
27.68	65.8	29.01	58.7	29.92	71.0
18.26	59.3	19.16	46.0	20.57	66.2
9.78	52.3	11.43	31.2	11.35	61.1
7.22	49.6			6.21	57.7
3.00	40.8			2.313	52.2
				.718	41.1

TABLE 2 -*Concluded*

C	*t*	*C*	*t*	*C*	*t*
Chloroform		Diethyl ether		Water	
	degrees C		*degrees C*		*degrees C.*
100.00	110.3	100.00	110.3	100.00	110.3
89.30	104.1	91.90	106.2	Forms a triple point at 79.6°C. over an undetermined range	
79.80	98.0	79.70	99.9		
76.90	96.0	70.03	95.2		
61.70	83.2	60.55	90.4		
52.90	74.1	47.72	84.6		
45.42	64.8	35.90	80.0		
35.65	50.7	24.96	76.0		
28.11	38.2	12.85	70.8		
21.00	22.1	5.900	63.4	0.380	69.0
		2.288	48.7	0.1743	43.3
		1.146	27.7		
		Ideal			
		100.00	110.3		
		90.00	105.0		
		80.00	99.2		
		70.00	92.9		
		60.00	85.8		
		50.00	77.9		
		40.00	68.4		
		30.00	57.2		
		20.00	42.4		
		10.00	20.1		

EXPERIMENTAL RESULTS

The experimental measurements of the solubility of acetyl-*o*-toluidine are listed in table 2, *C* being the molal percentage of the solute ($C = 100\,N$, where N is the mole fraction of the solute) and *t* the temperature in degrees Centigrade. The thermometers used were checked against thermometers calibrated by the Bureau of Standards. All readings were corrected for emergent stems.

The results marked "ideal" were calculated as will be explained in the next part of this paper. The results presented in table 2 were plotted on a large scale in terms of *C* versus *t*, and from these curves values of solubility have been obtained at 5-degree intervals of temperature. Table 3 was constructed from these values.

TABLE 3

Solubility of acetyl-o-toluidine in various solvents, interpolated at a series of temperatures, expressed in terms of mole percentage

TEMPERATURE	METHYL ALCOHOL	ETHYL ALCOHOL	*n*-PROPYL ALCOHOL	*n*-BUTYL ALCOHOL	ISOPROPYL ALCOHOL	ISOBUTYL ALCOHOL	BENZENE	CARBON TETRACHLORIDE	CHLOROFORM	ACETONE	DIETHYL ETHER
25	15.6	9.5	—	10.0	—	8.2	—	—	22.1	8.7	0.9
30	17.7	11.6	12.0	12.0	9.3	10.2	—	—	24.2	10.8	1.3
35	19.8	14.0	14.4	14.4	11.6	12.7	0.8	0.6	26.5	13.2	1.5
40	22.2	16.4	17.0	17.0	14.0	15.0	2.2	0.7	29.1	15.5	1.8
45	24.7	19.3	20.0	20.0	16.8	17.8	4.3	0.8	32.1	18.4	2.0
50	27.9	22.7	23.5	23.3	20.1	21.2	7.5	1.5	35.2	31.9	2.4
55	31.4	26.8	27.6	27.2	23.9	25.2	12.6	3.7	38.5	25.7	3.1
60	35.4	31.5	32.3	31.5	28.5	29.7	19.2	9.5	42.0	30.2	4.5
65	39.7	36.3	37.0	36.0	33.5	34.4	26.8	13.4	45.5	35.1	6.9
70	44.6	41.5	42.3	41.2	39.2	39.8	34.0	28.0	49.5	40.5	11.7
75	50.2	47.4	47.9	47.4	45.5	46.0	41.5	37.3	53.7	46.6	22.0
80	56.0	53.9	54.3	54.0	52.0	52.3	49.4	46.0	58.5	53.0	36.0
85	61.9	60.5	61.0	60.7	58.6	59.0	56.9	54.5	63.5	59.7	47.7
90	68.2	67.0	67.2	67.0	65.8	65.9	65.0	63.2	69.4	66.4	59.7
95	74.7	74.1	74.1	74.7	73.5	73.6	73.3	72.0	75.7	73.8	69.8
100	82.1	81.8	81.6	82.1	81.7	81.8	81.8	81.0	82.9	81.8	79.9
105	90.6	90.5	90.0	90.6	90.3	90.4	90.3	89.8	90.9	90.5	89.6
110.3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

DISCUSSION OF RESULTS

As far as could be determined, the heat of fusion of acetyl-*o*-toluidine has not been reported. It will be noted by inspection of the solubility curves (figure 1) that they all approach the melting point of the solute at approximately the same slope. Since a solution of the type studied here will be nearest to the ideal at high concentrations of the solute, it is reasonable to suppose that this slope is approximately the slope of the ideal solution curve. The molal heat of fusion was obtained from the slope of curves secured by plotting log N versus $1/T$ and by substitution in the usual ideal solubility equation,

$$\log N = \frac{-L_f}{4.58}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

where log N is the logarithm to the base 10 of the mole fraction of the solute, T_m is the melting point of the solute, T is the solution temperature of a particular system containing an amount of solute to give a mole fraction N, and L_f is the molal heat of fusion. In this way a large number of values were obtained ranging between 5500 and 5900 calories. The average of all values gives 5700 calories for the molal heat of fusion of acetyl-*o*-toluidine.

Using this value for the molal heat of fusion, the ideal solubility curve for acetyl-*o*-toluidine was calculated by solving for T for each 10 mole per cent from 10 to 100.

Figure 1 is a plot of part of the data of table 2. Since the curves for the alcohols are grouped so close together, only three are shown. The ideal curve is also shown. Figure 2 shows the curves for the alcohols on an enlarged scale over part of their range.

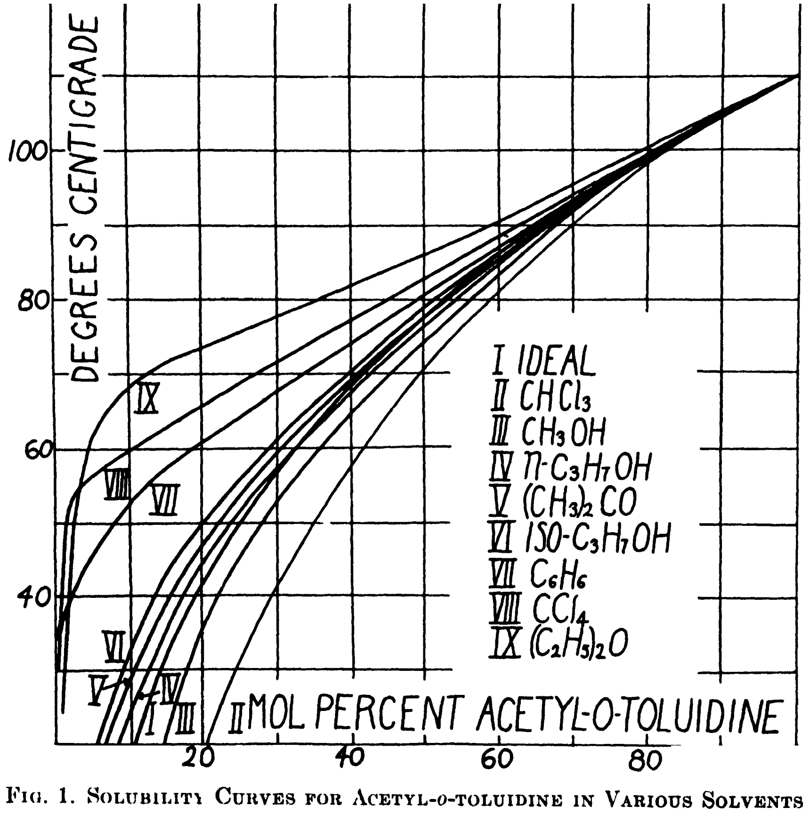

FIG. 1. SOLUBILITY CURVES FOR ACETYL-O-TOLUIDINE IN VARIOUS SOLVENTS

Except for methyl alcohol, the solubility curves for the alcohols and acetyl-*o*-toluidine form a very narrow band. This band is approximately coincident with the ideal curve above 60 mole per cent and shows increasing divergence below this point. Arrangement of the alcohols in descending order as to solvent power gives: methyl, propyl, ethyl, isobutyl, isopropyl. It is interesting to note that, of the alcohols studied, except methyl, propyl has the greatest solvent power, and isopropyl the least, while butyl had next to the greatest solvent power, and isobutyl next to the least. Evidently branching the carbon chain of the alcohol has a greater effect on the amount of acetyl-*o*-toluidine which it will dissolve than does the addition of an atom of carbon to the end of the chain. There is no evident relationship between the melting points of the alcohols and the rate at which the curves break or their relative positions on the sheet.

The curve for acetyl-*o*-toluidine and acetone is in the narrow band formed by the alcohol curves, being midway between the ethyl and isobutyl curves. This curve is very near to the ideal curve above 50 mole per cent. The dielectric constant of acetone is about of the same order as that of the alcohols and this may indicate that there is some relationship between the polarity and the solubility.

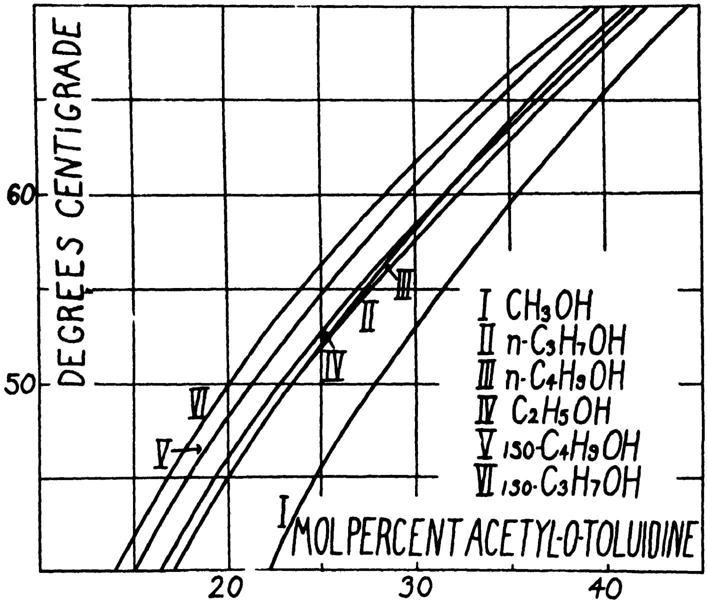

FIG. 2. SOLUBILITY CURVES FOR ACETYL-*o*-TOLUIDINE IN SEVERAL ALCOHOLS

The acetyl-*o*-toluidine was much more soluble in chloroform than in any other solvent studied. It is soluble to the extent of 23 mole per cent at 25°C. The curve is of the same general shape as the alcohol curves, but at low concentrations of solute it shows greater divergence from the ideal curve and the divergence is in the opposite direction. Its dielectric constant is not of the same order as that of the alcohols, being much lower.

The curve for carbon tetrachloride is rather unusual. It is almost exactly a straight line from 10 to 100 mole per cent of the solute. It is in this respect very different from the alcohols, acetone, and chloroform.

Acetyl-*o*-toluidine was less soluble in ether than in any other solvent studied except water. This curve, while nearly straight, shows slight reverse curvature at about 30 mole per cent. It breaks rather gradually below 15 mole per cent and crosses the carbon tetrachloride curve at 3 mole per cent and the benzene curve at about 1.5 mole per cent.

Acetyl-*o*-toluidine in water gives the phenomena of two liquid phases over a very wide range. It forms two liquid layers at about one-half mole per cent of solute and up to a concentration which has thus far not been determined exactly. No attempt was made to determine the critical solution temperature. The temperature of this triple point is near 79.6°C.

SUMMARY

The synthetic method has been used to determine the solubility of acetyl-*o*-toluidine in methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, chloroform, carbon tetrachloride, benzene, diethyl ether, and water.

The heat of fusion of acetyl-*o*-toluidine has been determined, and an ideal solution curve calculated and plotted.

REFERENCES

(1) Collett and Johnston: J. Phys. Chem. **30**, 70–82 (1926).
(2) Lazzell and Johnston: J. Phys. Chem. **32**, 1331–41 (1928).
(3) Collett and Lazzell: J. Phys. Chem. **34**, 1838–47 (1930).
(4) Walker, Collett, and Lazzell: J. Phys. Chem. **35**, 3259–71 (1931).
(5) Reference 3, p. 1839.

STUDIES ON ADSORPTION

The Relation of Water Held by Charcoal at Zero Pressure to the Ash Content

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In the past it has been generally accepted that the quantity of water adsorbed at zero pressure is dependent on the ash content. In the view of the author this is incorrect unless the ash should prove to be definitely hygroscopic. This probably only occurs to a very slight extent even with phosphoric acid activated charcoals, for the charcoal has been activated at a high temperature and most of the hygroscopic salts would therefore fuse, thereby losing this property to a large extent.

As a result of a number of experiments carried out recently, the author is in a position to suggest a more probable theory to account for the varying amounts of water which are held at zero pressure.

EXPERIMENTAL

The charcoals used in the present series which have been previously described are given in table 1. The remainder of the twenty-five charcoals are fully described in table 2.

Samples of these charcoals which had been previously employed in a study of the effect of activation on the isothermal and its relation to water hysteresis (1), were ashed by the following method, which was devised to prevent any loss of ash due to sublimation. The apparatus is shown in figure 1 and consisted of a silica U-tube A, fitted with two ground glass connections, B and C, which were closed by taps.

The general procedure was as follows: The charcoal under examination was heated for 1½ hours in an air oven at 150°C., this temperature being the most suitable for removing the greater part of the adsorbed water without altering the nature of the charcoal surface, and about 2 g. of it was packed into the apparatus, which had been previously cleaned and weighed. The cups D and E were then filled with Everett's wax and the whole reweighed. The charcoal was finally dried by passing dry air at 150°C. through the apparatus at 400 cc. per minute. It was then cooled and weighed. The ashing was carried out in the following manner. The U

TABLE 1

Charcoals used in this series and described previously

CHARCOAL	REFERENCE
A	J. Phys. Chem. **32**, 441 (1928)
B	J. Phys. Chem. **32**, 441 (1928)
C	J. Phys. Chem. **32**, 441 (1928)
D 1	Proc. Roy. Soc. London **130**, 610 (1931)
G	J. Soc. Chem. Ind. **47**, 372 T (1928)
L	J. Phys. Chem. **34**, 2202 (1930)
M 1	J. Phys. Chem. **34**, 2202 (1930)
M 2	J. Phys. Chem. **34**, 2202 (1930)
M 3	J. Phys. Chem. **34**, 2202 (1930)
M 4	J. Phys. Chem. **34**, 2202 (1930)
N	Proc. Roy. Soc. London **132**, 460 (1931)

TABLE 2

Other charcoals used in this study

CHARCOAL	APPARENT DENSITY	STARTING MATERIAL	ACTIVATING AGENT
E 1	0.349	Coal	Steam
F 1	0.534	Coconut shell	Steam
K 1	0.311	Peat	Phosphoric acid
L 1	0.445	Beechwood	Steam
M 5	0.404	Palm nut shell	Steam
M 6	0.392		
M A	0.427	Brazil nut shell	Steam
M B	0.60	Coconut shell	Steam
N 1	0.416	Almond shell	Zinc chloride
P	0.329	Peat	Zinc chloride
Q	0.294	Peat	Zinc chloride
R	0.379	Peat	Steam
S	0.250	Soft wood	Air
T	0 338	Peat	Zinc chloride

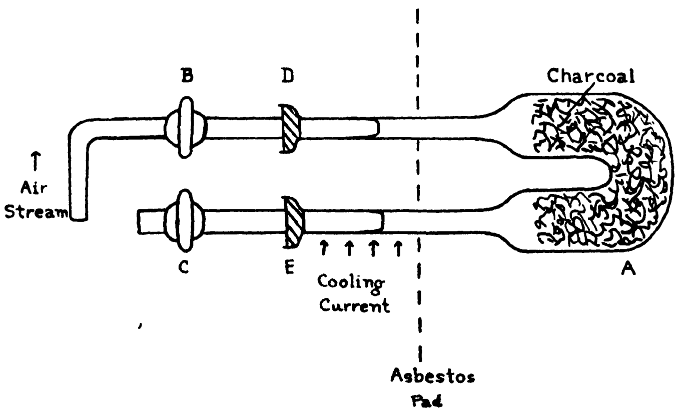

Fig. 1

portion was heated to a bright red heat, the rest of the apparatus being protected by an asbestos pad. Dry air was passed through the limb B at 20 cc. per minute, the exit tube C being cooled with a jet of ice-cold water.

TABLE 3

CHARCOAL	ASH (1)	ASH (2)
	per cent	*per cent*
A	3.98	3.92
N	0.67	0.61
Q	1.65	1.65

TABLE 4

CHARCOAL	PER CENT ASH	WATER AT ZERO PRESSURE	CARBON TETRACHLORIDE AT 0.01 MM PRESSURE
		milligrams per gram	*milligrams per gram*
A	3.95	15.4	93.0
B	4.03	2.0	57.0
C	2.72	17.5	145.9
D 1	1.81	2.7	116.4
E 1	20.5	2.1	61.0
F 1	3.70	9.0	134.1
G	7.07	2.5	121.9
K 1	27.3	27.1	57.5
L	9.27	18.1	149.7
L 1	6.22	23.8	137.0
M 1	1.17	5.0	4.0
M 2	1.17	26.1	111.6
M 3	1.17	32.9	152.0
M 4	1.17	19.1	143.1
M 5	1.17	19.3	129.6
M 6	1.17	12.2	125.2
M A	6.79	10.1	96.6
M B	1.43	1.0	125.0
N	0.64	12.7	71.4
N 1	0.83	36.3	75.3
P	3.59	2.0	128.5
Q	1.65	10.2	41.9
R	13.1	31.2	122.7
S	3.80	25.2	54.3
T	2.30	25.1	46.0

The ashing was continued until constant weight was attained, the degree of reproducibility of these results being shown by the duplicate experiments (see table 3).

The results of the ash determinations are expressed in table 4, together with the quantities of water held at zero pressure and of carbon tetrachloride at 0.01 mm., which latter results were obtained by employing an air-stream method, in order that as much H_2O might be retained on the charcoal surface as possible. In previous work it has been shown that there is excellent agreement between the air stream and vacuum techniques. In this case zero pressure is assumed when there is no loss in weight by passing dry air at 400 cc. per minute for 6 hours. As the water isothermal below 1 mm. is almost parallel to the pressure axis, it follows that the weight figure obtained corresponds to that of zero pressure within experimental error.

DISCUSSION

An examination shows that there is no great variation in the qualitative analysis of the ash of the various charcoals, except in cases where there has been chemical activation or a briquetting agent employed, hence it would appear that there is not sufficient variation in the composition of the ash to account for the various amounts of water which are chemically held.

Again reference to table 4 shows no obvious connection between the ash and the water held at zero pressure. In the series M 1 to M 6, which represents increasing stages of activation, the ash content is constant within experimental error, whereas the quantity of water varies between 5 mg. per gram and 32.9 mg. per gram. Therefore 1 mg. of ash retains 2, 3, 1.5, 1.5, and 1 mg. of water in the cases of M 2, M 3, M 4, M 5, and M 6, respectively. Again N 1 has 36 3 mg. per gram of water tightly held but only 0.83 per cent ash, which would involve 1 mg. ash adsorbing approximately 4.5 mg. of water, sorption of this order being unknown by any substance. In the case of N, 1 mg. of ash adsorbs 2 mg. of water at zero pressure. A sugar charcoal, J, has been found to have 5.4 mg. per gram of water retained at zero pressure (2), although the ash content was 0.1 per cent. This water cannot be retained by the ash, as this would involve 1 mg. of ash adsorbing 5 mg. of water.

Further data have been obtained from the series of measurements on the sorption of water vapor by activated charcoal carried out by Allmand and his coworkers (3). In two experiments carried out with charcoal B, the quantities of water held at zero pressure were 4 mg. per gram by the static and 12 mg. per gram by the air-stream method, the temperature of evacuation, 270°C., being the same in both cases. A comparison of data for charcoals A and C can best be made in tabular form (see table 5), the general trend of which results would be the same if experiments had been carried out at neighboring temperatures.

This is interesting since the ash is 3.95 per cent for A and 2.72 per cent for C, yet the quantities of water fall in the same order under similar conditions. It is impossible to imagine that the same percentage of ash is removed in each charcoal under the same conditions of experiment, which would follow if the water depended on the ash content.

From data such as these it is obvious that the ash content cannot account for the quantity of water held at zero pressure. It has already been shown (4) that water is adsorbed both by the active centers and in a quasi chemical form by the C_xO_y which is always present to a greater or lesser extent on the charcoal surface, the amount depending on the type of charcoal and the treatment to which it has been subjected. This water is held at zero pressure and can only be removed if the C_xO_y complex is broken up. Again the greater the number of active centers on the charcoal surface the greater will be the amount of water held by the free valencies of the exposed carbon atoms, i.e., the greater will be the amount of water tightly held. As a result of a new theory of activation of charcoal (5) it is possible to predict how the water content at zero pressure should alter during the course of a sorption experiment. If a large amount of C_xO_y is present at the commencement a large quantity of water will be sorbed at zero pressure. Some of the more loosely held C_xO_y is slowly removed by the water, thereby causing the quantity of sorbed vapor to drop somewhat. As the C_xO_y is removed from the active points more water will be adsorbed at zero pressure. Hence one would expect a large amount of water to be adsorbed at zero pressure at first, then less, and finally an increased amount again during the course of the experiment. If the bulk of the water is held by the active centers the figures for the amount of water held at zero pressure should bear the same ratio to the carbon tetrachloride figures at 0.01 mm. in each case, since carbon tetrachloride is firmly held at this pressure at room temperature. This was not found to be the case, although the

TABLE 5

Comparison of data for charcoals A and C

METHOD	TEMPERATURE OF EVACUATION	CHARCOAL A	CHARCOAL C
	degrees C	*milligrams per gram*	*milligrams per gram*
Nitrogen stream	800	44	40
New dynamic*	—	15	18
Nitrogen stream	270	13	14
Static	800	8	10
	270	4	6
NaOH extracted	800	3	2
Oil stream	270		10
	800		23

* Unpublished work by the author.

M 1 to M 6 series shows a definite rise and fall both for water and carbon tetrachloride (table 4). As the result of further work on the sorption of vapor by unactivated charcoal (4) this is an inevitable result, since water can be adsorbed at any active center, on the C_xO_y sponge or at any other point on the charcoal surface, whereas carbon tetrachloride, being a typical non-polar vapor, can only be adsorbed at the active centers. The presence of C_xO_y, which, as has already been stated, is always present to a greater or lesser extent, increases the amount of water sorbed but decreases the quantity of carbon tetrachloride, owing to a poisoning effect. This latter state is shown very markedly when an isothermal on charcoal A, after evacuation at 110°C. (6), is compared with a similar isothermal after evacuation at 800°C. (7). At low pressures the quantity in the latter case is almost twice that of the former, owing entirely to the removal of C_xO_y from the active centers.

TABLE 6

CHARCOAL	APPARENT DENSITY	SAT Q AT 115 MM	WATER AT ZERO PRESSURE
		milligrams per gram	*milligrams per gram*
M 1	0.620	12	5
M 2	0.584	376	26
M 3	0.478	682	33
M 4	0.477	729	19
M 5	0.404	892	19
M 6	0.392	920	12

TABLE 7

Comparison of coconut charcoals

CHARCOAL	APPARENT DENSITY	CARBON TETRACHLORIDE Q AT 115 MM	WATER AT ZERO PRESSURE
		milligrams per gram	*milligrams per gram*
M B	0.60	307	1.0
D 1	0.575	301	2.7
F 1.	0.534	424	9.0
C	0.490	647	17.5

In some unpublished work it has been found possible to arrange the charcoals according to the degree of activation, which is the order in which the carbon tetrachloride saturation values fall at 115 mm. at 25°C., the highest figure corresponding to the greatest activation. The data for the series M 1 to M 6 are given in table 6.

This series forms the best for comparison because the starting material is exactly the same in each case, the degree of activation alone being altered All samples before activation should have more or less the same C_xO_y content As the latter proceeds, the amount of water held by the active centers will increase, hence the water content at zero pressure should be strictly comparable with the degree of activation, giving a fall followed by a rise

Finally as the charcoal becomes overactivated the quantity of water will fall

In table 7 comparison is made between coconut charcoals obtained from different sources In this case also the agreement is good. One cannot compare data for the briquetted charcoals, which includes all the peat charcoals, as well as L, and L 1, since the degree of compression of the material alters as well as the degree of activation

SUMMARY

A number of ash determinations have been carried out on different charcoals, and a comparison made with the amounts of water held at zero pressure

An examination of other available data has been made

A theory has been advanced to account for this variation in the quantity of tightly held water, in which it has been suggested that the ash plays no part in the retention of the water at zero pressure, but that the latter is held in a quasi chemical manner by the active centers and C_xO_y complex.

REFERENCES

(1) Accepted by the Faraday Society for publication
(2) Allmand, A J, Hand, P G T, Manning, J E, and Shiels, D O. J Phys. Chem **23,** 1682 (1929)
(3) Allmand, A J, Hand, P H T, Manning, J E, and Shiels, D O J Phys Chem, 1928–1929
(4) Burrage, L J Trans Faraday Soc **29,** 458 (1933)
(5) Burrage, L J Trans Faraday Soc **29,** 445 (1933)
(6) Allmand, A J, and Chaplin, R Proc Roy Soc London **129A,** 235 (1930)
(7) Allmand, A J, and Puttick, A Proc Roy Soc London **130A,** 197 (1930)

THE SYSTEM SODIUM DISILICATE–SODIUM FLUORIDE

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The ternary system $Na_2O \cdot SiO_2 \cdot NaF$ has been shown to be of fundamental importance in the composition of porcelain (vitreous) enamels. Two of the binary systems contained in the above ternary system have been published, namely, sodium oxide–silica (1) and sodium metasilicate–sodium fluoride (2). This paper describes the study of the system sodium disilicate–sodium fluoride. This is of particular interest to enamelists in view of the suggested use of sodium silicates as a raw material (3), especially since the disilicate contains a high per cent of silica (66.0 per cent) and has a low melting point (874°C.).

The preliminary study (2) of this system showed that difficulties would be encountered owing to the very small heat arrests and the sluggishness of the disilicate in attaining equilibrium. However, by using a special recording potentiometer and supplementing this continuous record with differential readings taken at least every 30 seconds, the breaks could be readily detected. In this way we were able to obtain the data without using the tedious and somewhat less accurate quenching methods.

EXPERIMENTAL PROCEDURE

Chemicals

Some of the silica was obtained from large clear quartz crystals. The foreign matter was scraped off and the crystals boiled in aqua regia. After being thoroughly washed they were placed in a large platinum dish, heated, then suddenly chilled by a stream of cold distilled water. This shattering process was continued until the pieces became small. They were then ground to a powder in an agate mortar.

The other pure silica was from commercial powdered quartz. After a water wash to remove any lint it was boiled three times with hydrochloric acid and twice with aqua regia, followed by a thorough water washing.

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[1] Holder of the Cushman Fellowship for Fundamental Research in Vitreous Enamels, 1930–1931.

[2] Holder of the Cushman Fellowship, 1931–1934.

Both of these samples were then dried in an electric oven at 120°C. On treatment with hydrofluoric acid they gave, respectively, 0.03 and 0.04 per cent residue.

The sodium oxide content was obtained by using C.P. sodium carbonate monohydrate, which by conversion to the sulfate was shown to be 99.90 per cent pure.

Merck's C.P. sodium fluoride was recrystallized twice from water, dried in platinum in an electric oven, and by conversion to the sulfate was found to be 99.00 per cent sodium fluoride. This sample contained 0.80 per cent water.

The sodium disilicate was made by fusing the calculated amounts of sodium carbonate monohydrate and silica in covered platinum crucibles, in a small electric furnace. Since the high viscosity of the disilicate prevented it from being poured, the outside of the crucible was chilled with a stream of cold water. This caused the melt to crack enough so that it could be removed. The material was then ground to a powder in an agate mortar This was re-fused and re-powdered until it became homogeneous.

Apparatus

The furnace (2) was a vertical resistance furnace, having two windings, an inner one of platinum-20 per cent rhodium alloy wire and the outer of Chromel resistance wire. 110 volts A.C. was used on both coils, the current being controlled by two water-cooled rheostats.

The thermocouple was a standard platinum and platinum-10 per cent rhodium couple. A differential junction surrounded by a platinum-covered nickel "neutral body" of approximately the same heat capacity as the platinum crucible and melt was suspended about 6 cm. above the melting point junction. The melting point crucible was a heavy cylindrical, platinum crucible, 5 cm. high and 1.6 cm. in diameter. The thermocouples and supports for holding the crucible were in a single unit which could be raised and removed from the furnace.

The heating curves were obtained with a specially designed Leeds and Northrup "Micromax" recording potentiometer. This recorder balances every second and has a paper speed of sixteen inches an hour. The temperature can be read to ± 0.5°C. from 500°C. to 1200°C.

The differential temperature readings were made with a "student type" potentiometer and a "wall type" galvanometer. At every reading of the differential temperature a mark was made on the recorder paper by means of an electrically controlled pen. In this way the differential curve could readily be plotted on the recorder sheet.

Preparation and melting points of mixtures

The various mixtures were prepared by weighing out theoretical amounts of the disilicate and sodium fluoride, mixing thoroughly, fusing slowly in a small electric furnace, then chilling rapidly, as mentioned previously. After being ground to a powder each was re-fused and again powdered in order to obtain a homogeneous mixture.

To obtain a melting point, this powder was introduced into the crucible, the thermocouple inserted, and the entire unit placed in the furnace. It was rapidly heated to above the melting point of the mixture, and allowed to cool slowly, so that crystallization could take place. The furnace was then heated again, this time slowly, and both the melt and the differential temperatures were recorded. After the melting point was reached the furnace was again cooled slowly. Only heating curves were taken, as the mixture always undercooled before crystallizing. In every case at least three checks were obtained on both the solidus and liquidus points.

It is difficult to obtain sharp breaks by the usual method of thermal analysis in the sodium disilicate region. However, by carefully controlling the rate of heating of the furnace and taking a continuous melting point record and simultaneously taking the differential readings, the breaks in the heating curve could be easily detected and duplicated. The thermocouple was checked before and after every melting point. The standards used were sodium chloride (800.4°C.) (4) and sodium metasilicate (1089°C.) (1).

In a number of cases the melts, after being used for a melting point determination, were powdered and weighed; definite quantities of either the disilicate or sodium fluoride were then added. The melting points of such mixtures were identical with those of the mixtures of like composition prepared by mixing only the disilicate and sodium fluoride. This indicates that the melt does not change in composition on being fused.

RESULTS

The data obtained are given in table 1 and plotted in figure 1. The system is a simple V eutectic type, no compounds being formed. The eutectic composition is 39.5 ± 0.1 mole per cent of sodium fluoride and the eutectic temperature is 797°C. ± 1°C.

The melting point of the disilicate was found to be 874°C., agreeing with the value obtained by Kracek (1).

The solidus disilicate relations have been shown by Kracek (1) to be very complex. At present the solidus relations for the system sodium disilicate–sodium fluoride below the eutectic temperature have not been studied sufficiently to enable one to draw any definite conclusions.

TABLE 1

The system sodium disilicate-sodium fluoride

POINT NO	MOLE PER CENT SODIUM FLUORIDE	WEIGHT PER CENT SODIUM FLUORIDE	TEMPERATURES	
			Liquidus	Solidus
			degrees C	*degrees C*
1	0 00	0 00	874	
2	10 00	2 50	861	799
3	20 00	5 45	850	796
4	32 52	10 00	825	797
5	39 50	13 09	797	797
6	42 10	14 36	817	799
7	47 04	17 00	870	798
8	53 00	20 64	915	799
9	59 11	25 00	946	796
10	70 00	34 98	973	797
11	81 14	49 80	985	802
12	90 97	69 91	988	793
13	96 06	84 90	991	798
14	100 00	100 00	995	

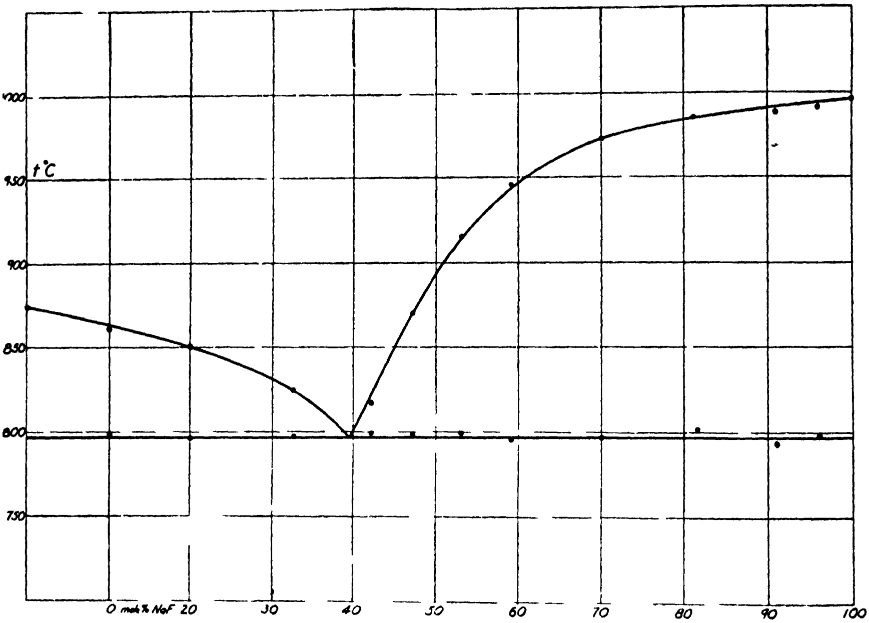

Fig 1 The System Sodium Disilicate-Sodium Fluoride

SUMMARY

The system, sodium disilicate–sodium fluoride, is a one eutectic type and the eutectic occurs at a composition 39.5 ± 0.1 mole per cent of sodium fluoride and at a temperature of 797°C. ± 1.0°C.

REFERENCES

(1) KRACEK, F. C.: J. Phys. Chem. **34**, 1583 (1930).
(2) BOOTH AND STARRS: J. Phys. Chem. **35**, 3553 (1931).
(3) MANSON, M. E.: J. Am. Ceram. Soc. **14**, 490 (1931).
(4) International Critical Tables, Vol. I, p. 54. McGraw-Hill Book Co., New York (1926).

THE CRYSTAL STRUCTURE OF $CaSO_4 \cdot CO(NH_2)_2$

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During the course of studies on salt–urea systems Dr. C. W. Whittaker (1) of this laboratory prepared a well-crystallized material which upon analysis proved to be a urea "coordination" compound of calcium sulfate. Preliminary optical examination showed that the crystals have an unusually high birefringence, approaching that of urea itself. This predicated a sufficiently interesting underlying crystal structure to warrant a thorough study. Considerable importance, moreover, attaches to this compound as one possibly formed in some fertilizer mixtures.

Crystal structure determinations of a number of hydrates and ammoniates have shown the essential validity of Werner's coördination theory as applied to polar, but uncharged, groups. No attempt, however, has yet been made to find the structure of a coordination compound containing urea, ethylene diamine, or pyridine, etc. This hesitancy has been well based on the knowledge that these large molecules might place insuperable barriers in the way of the analyst and leave him with nothing more than a space group determination for his efforts.

The analysis of urea coordination compounds holds some hope when the importance of the inherently high anisotropy of the urea molecule is fully realized. In the case of $CaSO_4 \cdot 4CO(NH_2)_2$ the optical properties proved to be an unerring guide through the complexities of an unusually complex triclinic crystal. The structure found is perhaps sufficiently accurate to serve as the basis of a future more elaborate analysis. It holds some additional interest in being the first triclinic ionic compound to have yielded its essential crystal structure.

CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES

In general the crystals were elongated prisms (0.5 x 0.5 x 1 mm.) showing predominant development of the p faces, figure 1, with only the forms a, b, c, p_1, and p_2 present. Two crystals with the x faces developed were measured on the optical goniometer. The results together with the calculated crystallographic constant are given in table 1.

A small fraction of the crystals were found to be twinned on (001). One specimen was measured on the universal stage under the microscope. The spherical projection of the twin axis was obtained from the point of intersection of the three great circles connecting in order the projections of the principal directions of the optical ellipsoids of the two crystals. The twin axis was found to be either the *b* axis or the normal to the *b* face A second specimen, giving moderately bright signals from the *p* faces, was measured on the optical goniometer. The results, which are summarized in table 2,

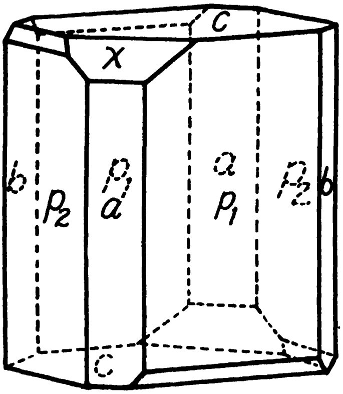

FIG. 1. A TYPICAL CRYSTAL OF $CaSO_4 \cdot 4CO(NH_2)_2$

TABLE 1

Goniometric measurements

FORM		ρ	φ	LIMITS OF OBSERVATIONS		FACES MEASURED
				ρ	φ	
100	*a*	90°1′	93°12′	90°0′ to 90°2′	93°12′ to 92°56′	4
110	p_1	90°2′	47°3′	90°0′ to 90°2′	47°2′ to 47°4′	4
010	*b*	90°1′	00°0′	90°0′ to 90°2′	359°50′ to 0°10′	4
$\bar{1}10$	p_2	90°0′	136°10′	90°0′ to 90°0′	136°7′ to 136°10′	4
001	*c*	2°9′	9°58′	2°4′ to 2°14′	9°56′ to 9°60′	2
101	*x*	41°30′	90°39′	41°28′ to 41°32′	90°35′ to 90°43′	2

$\nu = 93°9'$ $\mu = 89°45'$ $\lambda = 87°53'$

$\alpha = 92°6'$ $\beta = 90°22'$ $\gamma = 86°50'$

$$p_0 : q_0 : r_0 = 0\,8796 : 0.8658 \;.\; 1$$

$$a : b : c = 0\,9836 : 1 : 0.8645$$

Clear signals were obtained only from forms p_1 and p_2 These were accordingly given infinite weight in calculating ν and p_0'/q_0'. The value of α is particularly sensitive to ρ for 001 and therefore is likely to be considerably in error.

Forms observed *a*, (100), *b* (010), *c* (001), p_1 (110), p_2 ($\bar{1}10$), *x*, (101), ($1\bar{1}1$), (111), ($\bar{1}\bar{1}1$), ($\bar{1}11$), ($\bar{1}01$).

Cleavage absent.

The face development indicates that the crystals are holohedral.

show that the twin axis is the crystallographic *b* axis and that the composition plane is (001). A number of crystals apparently twinned in other manners were examined on the universal stage and in every instance were shown to be either parallel growths or unrelated crystals closely adhering to one another.

The indices of refraction measured under the microscope by the immersion method for Na_D light are at 25°C.:

$$\alpha = 1.523, \beta = 1.583, \gamma = 1.615$$

The experimental error does not exceed ±0.002. The crystals are optically negative with $2V$, calculated, 70.0°.

TABLE 2

Goniometric measurements on a twinned crystal mounted on $(00\bar{1})$

The V scale has been inverted to agree with the previous crystallographic description

FORM		ρ	φ	FACES
		Crystal No. 1		
$\bar{1}10$	p_2	90°2′ to 90°4′	136°9′ to 136°10′	2
010	b	90°0′ to 90°4′	359°45′ to 359°46′	2
110	p_1	90°4′ to 90°6′	47°1′ to 47°7′	2
100	a	90°4′ to 90°0′	92°40′ to 92°57′	2
		Crystal No. 2		
110	p_1	88°55′ to 89°00′	315°20 to 315°22′	2
010	b	87°57′ to 88°3′	358°53′ to 359°13′	2
$\bar{1}10$	p_2	88°14′ to 88°16′	46°16′ to 46°19′	2
100	a	89°40′ to 90°22′	93°9′ to 93°13′	2

The measurements on ρ of the two members of the same form are reduced to comparable values. Signals, not very clear, were obtained only from forms p.

The orientation of the optical ellipsoid was determined by measurements on the universal stage. The crystals were mounted in an ethylene glycol–phthalic anhydride plastic between hemispheres with $n_D = 1.557$ The average results, uncorrected for differences in refractive indices, obtained from a number of crystals are summarized in figure 2. The irregular lines indicate the magnitude of the observational errors. The observed value of $2V$ is 70°, agreeing with the value calculated from the indices of refraction.

X-ray diffraction data

Rotating crystal and Weissenberg photographs were made with the crystallographic axes as axes of rotation. Copper K radiation was used throughout with a camera radius of 5.01 cm.

The lattice dimensions were calculated from the layer line separations. The angles between the axes of the reciprocal lattice and the values of p_0, q_0, and r_0 were determined from the equatorial zone Weissenberg photographs. The linear elements calculated from these measured quantities are listed in table 3. The values obtained from the x-ray diffraction and optical goniometric data agree very closely save in the case of α, in which instance the goniometric value is suspect.

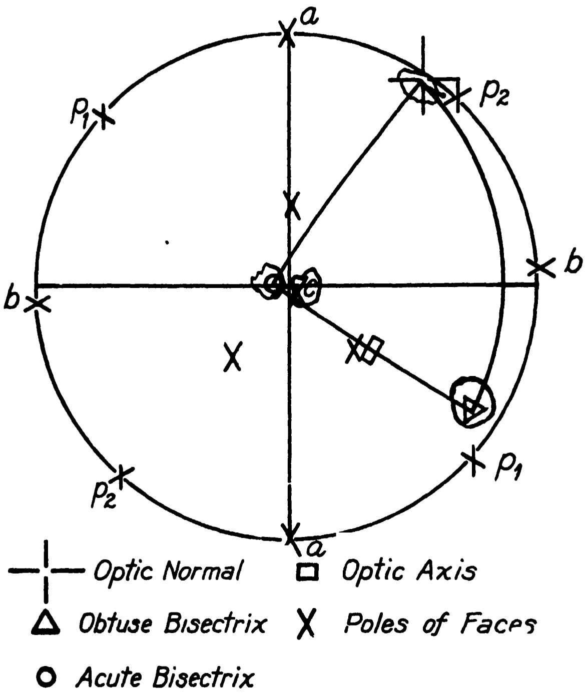

Fig. 2. Stereographic Projection Showing the Optic Orientation of $CaSO_4 \cdot 4CO(NH_2)_2$ as Determined on the Universal Stage

The projection of the c axis is at the center of the figure

Weissenberg photographs were made from four of the layer lines. In these cases the slit was rotated making $\sin \beta = \sin \mu$ (2) so that the axis of rotation would lie on the reflection sphere. The absence of symmetry around the central image confirmed the triclinic character of the crystals.

The intensities of some of the observed reflections are summarized in tables 4 to 9. *A most striking characteristic of these data is that many types of planes are either absent or are represented by only a few of the possible reflections.* The observations can be divided into two classes (σ denotes odd; e, even):

Strictly absent	*Approximately absent*
$(\sigma 00)$, $(0\sigma 0)$	(00σ)
$(\sigma e0)$, $(e\sigma 0)$	$(\sigma\sigma 0)$
$(0\sigma l)$, $(\sigma 0l)$	$(0k\sigma)$, $(h0\sigma)$
$(e\sigma l)$, (σel)	$(ee\sigma)$, $(\sigma\sigma e)$

The data from Weissenberg photographs of the third and fourth layer lines are summarized in tables 7 and 8. It can be seen that reflections are

TABLE 3

Summary of crystallographic constants

	WEISSENBERG X-RAY	GONIOMETER OPTICAL
a_0 from layer	14 74	
b_0 line	14 95	
c_0 separation	6 47	
γ^*	93°18′	93°9′
α^*	88°36′	87°53′
β^*	89°42′	89°45′
α	91°26′	92°8′
β	90°22′	90°22′
γ	86°42′	86°50′
p_0	0 4395	0 8796
q_0	0 4326	0 8658
r_0	1	1
a	0 9859	0.9836
b	1	1
c	0 4327	0 8645
Density (observed)	1 8006	
Density (calculated)	1 820	

TABLE 4

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Equatorial zone, *a*, axis of rotation. All planes with *k* odd are strictly absent; the only reflections from planes with *l* odd are listed in table 9

	$0k2$	$0k4$	$0k6$	$0k\bar{2}$	$0k\bar{4}$	$0k6$
$00l$	v s.*	v.w.	v.w.	v.s.	v.w.	v.w.
$02l$	s.	a.	w.	?	v.w.	m.w.
$04l$	m.s	m.s.	m.w.	m s.	m.	m.w.
$06l$	w.	m.w.	w.	m.w.	w.	m.w.
$08l$	m.	m.	v.w.	m.	m.	w.
$0\ 10.l$	m	w.	a.	m.	m.w.	
$0\ 12.l$	m.w.	m.		m.w.	m.w.	
$0\ 14.l$	m w.	m.w.		v.w.		
$0\ 16\ l$	w.	w.		w.		

* The following abbreviations are used: v.s., very strong; s., strong; m.s., medium strong; m., medium; m.w., medium weak; w., weak; v.w., very weak.

present only from ($\sigma\sigma\sigma$), ($ee\sigma$), and ($\sigma\sigma e$). Weissenberg photographs were made from the second layer lines with *c* and with *b* as the axes of rotation. Complete indices were not assigned in these cases, since positive and negative values were not differentiated, but it could be seen that planes (σ21), ($e\sigma$2), and (σe2) were strictly absent and ($e2\sigma$), ($\sigma\sigma$2) approximately so. Laue photographs were made with the incident beam (*W* general radiation, 26,000 *V* peak) parallel and at slight angles to the *b* axis. Reflections in the first order ($n\lambda$ = 0.48 to 0.96 A.U.) were obtained only from ($\sigma\sigma\sigma$),

TABLE 5

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Equatorial zone, *b*, axis of rotation. All planes with *h* odd are absent; the only reflections from planes with *l* odd are listed in table 9

	$h02$	$h04$	$h06$	$h0\bar{2}$	$h0\bar{4}$	$h0\bar{6}$
$20l$	m.s.	m.	v.w.	s.	a.	v.w.
$40l$	m.	m.	m.w	m.	m.	w.
$60l$	m.w.	m.w.	m.	w.	m.	v.w.
$80l$	m.s.	m.	m.w.	w.	m.w.	w.
$10.0.l$	m.s.	v.w.	a.	m.w.	a.	
$12.0.l$	w.	w.		m.w.	w.	
$14.0.l$	w.			m.w.		
$16.0.l$	m.					

TABLE 6

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Equatorial zone, *c*, axis of rotation. All planes with *h* or *k* odd are absent save the few *h* and *k* odd listed in table 9

	$0k0$	$2k0$	$4k0$	$6k0$	$8k0$	$10.k.0$	$12.k.0$	$14.k.0$
$h00$		v.s.	s.	a.	m.s.	v.w.	v.w.	m.w.
$h20$	v.s.	m.	m.	a.	w.			
$h40$	m.s.	v.s.	m.s.	m.	a.			
$h60$	w.	w.	m.s.	v.w.	a.			
$h80$	s.	a.	m.	m.	m.			
$h.10.0$	w.	a.	a.	v.w.	m.	m.		
$h.12.0$	w.	v.w.	m.w.	m.	m.			
$h.14.0$	a.	m.w.	w.					
$h.16.0$	m.w.	w.						
$h\bar{2}0$		m.	v.s.	w.	a.	a.	w.	m.w.
$h\bar{4}0$		m.s.	m.s.	m.s.	m.	v.w.	m.	w.
$h\bar{6}0$		a.	m.	m.w.	m.w.	m.	m.	
$h\bar{8}0$		m.w.	a.	m.w.	m.	m.s.	v.w.	
$h.1\bar{0}.0$		a.	w.	v.w.	w.	w.	w.	
$h.1\bar{2}.0$		a.	m.w.	m.w.	m.w.			

(σeσ), and (σσe), without particular differentiation in intensities between the three classes.

The odd layer lines on the rotating crystal photographs, while present in all cases, are far less prominent than are the even ones. Some strong reflections are present on the odd layer lines however, particularly for values of ξ less than 1.2. Some of these characteristics can perhaps be seen by an inspection of the typical photograph reproduced as figure 3.

TABLE 7

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Fourth layer line, *a* axis of rotation. All planes with *k* odd are strictly absent, the only reflections from planes with *l* odd are listed in table 9

	4l	4l 4	4l 2	4l 4	4l 2	4k 4
40l	m	m w	m s	m	m	m w
42l	v w	w	w	m w	m s	v w
44l	s	w	s	m w	s	w
46l	m s	a	w	a	m w	v w
4 8 l	w		m w	a	m w	m w
4 10 l	a		a		a	w
4 12 l	m w		m w		w	

TABLE 8

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Third layer line, *a* axis of rotation. All planes with *k* even are strictly absent

310 a	310 a	311 v w		311 v s	311 s
330 v w	330 a	331 v w	331 a	331 a	331̄ a
350 w	350 w	351 v w	351 a	351 m	351̄ w
370 v v w	370 v w	371 v w	371 w		371 a
390 w	390 a	391 m w	391 w		
3 11 0 a			3 11 1 a		
3 13̄ 0 a	312 w		312 w	313 w	313 a
3 15 0 w	332 m s	332 w	332 m	333 v w	333 w
	352 a	352 m w		353 w	
	372 a	372 a			
	392 a			314 w	315 w
	3 11 2 w				

Although unambiguous index assignments can only be made for Weissenberg and Laue photographs it can nevertheless be seen that none of the reflections of greater than medium intensity on the odd layer lines with *a* and *b* as axes of rotation had close to the same values of ξ as reflections on the two adjacent layer lines. Since the values of the angles, α, β, and γ are very close to 90° it follows that the planes giving reflections on the odd layer lines in general have different values of *h* and *l*, or of *k* and *l* than those present on the even layer lines. This then would be compatible with the presence chiefly of planes ($\sigma\sigma e$) and ($\sigma\sigma\sigma$), as borne out by the Weissenberg photographs of the layer lines. The subduing of the odd layer lines with c as the axis of rotation can be explained in the same manner

The density calculated on the basis of the unit of structure containing four $CaSO_4\ 4CO(NH_2)_2$ is 1 820. This value agrees with that determined by the centrifugal suspension method, 1.8006. The 1 per cent discrepancy arises chiefly from errors in the values of the fundamental lattice constants.

The space group is either $P1$, or $P\bar{1}$. The face development and the character of the signals indicate that the crystals belong to the holohedral division of the triclinic system. The derived structure, although isomorphous with $P\bar{1}$, does not depend upon the assumption of holohedry.

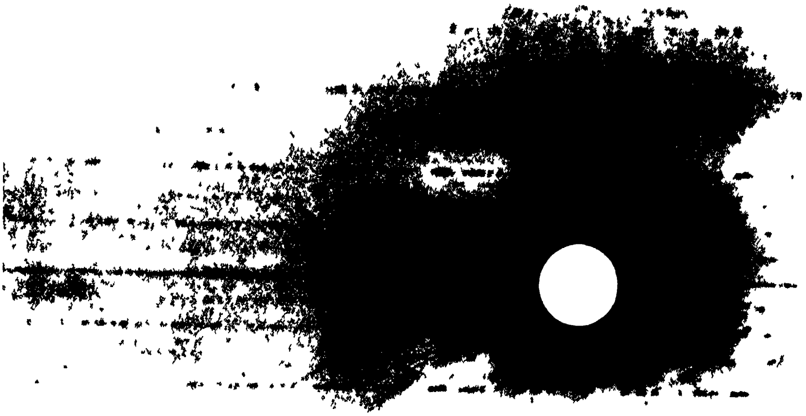

FIG. 3 ROTATING CRYSTAL PHOTOGRAPHS
Copper K radiation; a axis of rotation

THE STRUCTURAL AND OPTICAL PROPERTIES OF CALCIUM SULFATE AND UREA

The crystal structure of anhydrite, $CaSO_4$ (3), is known with sufficient accuracy to show that eight oxygen ions of sulfate groups are in the first coordination sphere around each calcium ion. In gypsum (4), as described at the present time, each calcium ion is surrounded by four oxygen ions of sulfate groups and two water molecules of closest approach. In calcium oxide and in the various silicates containing calcium the coördination number for oxygen ions has been found to be six, seven, or eight.

The most trustworthy value for the Ca^{++} to O^{--} distance for a coördination number of 6 is 2.40 A.U., as found for calcium oxide. For coördinations of 4 to 8 this value would be expected to be between 2.25 and 2.55 (5). The values observed in the various calcium silicates are close to 2.40, usually between 2.35 and 2.55. The sulfur to oxygen distance has not yet been determined in a sulfate. It is quite safe to assume, however, that it is the same as the phosphorus to oxygen distance in KH_2PO_4 (6), namely, 1.56 A.U., and that the oxygen ions are at the corners of regular tetrahedrons surrounding the sulfur ions.

The described structure of gypsum is of questionable accuracy since the calcium–oxygen distances are as small as 2.1 A.U. and since the first coördination sphere around calcium contains but six oxygen atoms, of which only four are ions. The structure is perhaps sufficiently accurate to indicate that the water molecules are near the calcium ions, the distances as given being 2.40 A.U. Consideration of a number of ammoniates and hydrates suggests that such polar groups approach to within about 2.80 A.U. of calcium ions, the limits of this value being very wide

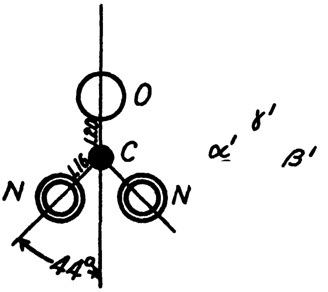

FIG. 4. THE INTERATOMIC DISTANCES IN A UREA MOLECULE

The centers of all the atoms are in the same plane. The directions of maximum, mean, and minimum polarizations are shown.

Inspection of the crystal structure of urea shows that the oxygen ends of the molecules are near the NH_2 groups of other molecules. The closest intermolecular distances of approach are: O to NH_2, 3.15 A.U. The properties of urea indicate that its molecules are polar, the NH_2 groups being positive with respect to the oxygen atoms.

In general the birefringence of sulfates R_2SO_4, RSO_4, or $R_2(SO_4)_3$ is low, since a regular tetrahedral grouping of isotropic resonators, such as afforded by a SO_4 group, is isotropic. The indices of refraction of anhydrite, $CaSO_4$, are $\alpha = 1.571$, $\beta = 1.576$, $\gamma = 1.614$, with the density, ρ equal to 2.93. In gypsum $\alpha = 1.520$, $\beta = 1.523$, and $\gamma = 1.530$ with $\rho = 2.32$. The birefringence of calcium sulfate formed by dehydrating gypsum at low temperatures is less than 0.015.

Urea crystallizes in the tetragonal system with $\alpha = \beta = 1.484$, $\gamma = 1.602$, and $\rho = 1.335$. The direction of maximum polarization is parallel to the twofold axes of the molecules. α and β are perpendicular to the plane of half the urea molecules and parallel to the planes of the other half. The optical properties of a lattice formed by the translation repetition of urea molecules can not satisfactorily be calculated at the present time. It is sufficient however to indicate, as permitted by elementary considerations, that α', β', and γ' would have the directions shown in figure 4, with β' somewhat smaller than γ' and α' very small compared to β' or γ'

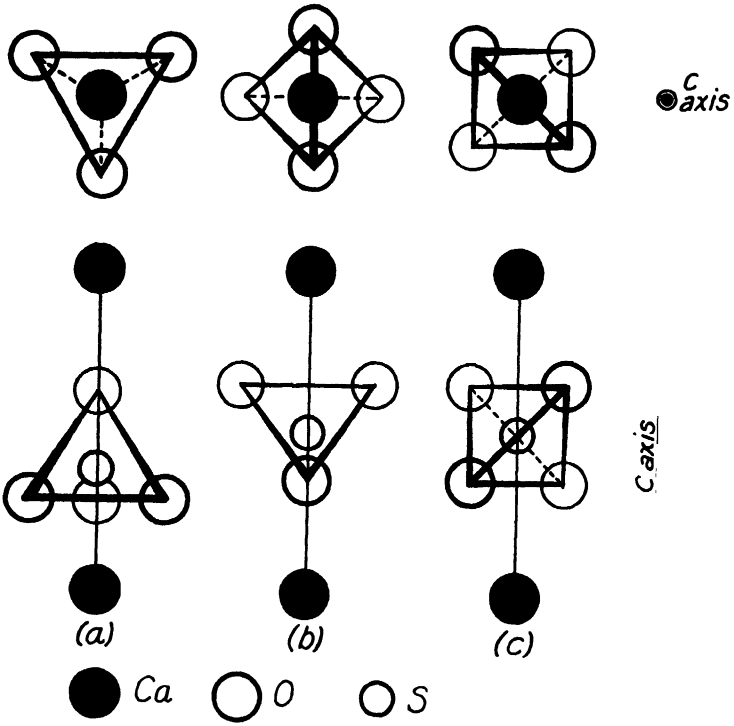

FIG. 5. POSSIBLE ARRANGEMENTS OF THE Ca^{++} IONS AND SO_4 GROUPS ALONG THE c AXIS OF $CaSO_4$ $4CO(NH_2)_2$

Rotations about the c axis are not determined. The calcium–oxygen distances are (a) 2.43 A.U., (b) 2.64 A.U., and (c) 2 68 A.U.

The crystal structure of $CaSO_4 \cdot 4CO(NH_2)_2$

The explanation of the many types of absent reflections affords the starting point for the structure determination. The lattice must approach very closely to being a face-centered one, particularly in the *a* and *b* directions. Each atom must have approximate translations of 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$. The calcium atoms can be placed in these positions without loss in generality.

The regular tetrahedral sulfate groups having sulfur to oxygen distances equal to 1.56 A.U. are to be placed within this lattice of calcium ions, in a manner such that the Ca^{++} to O^{--} distances are about 2.40 A.U. Fortunately, there are but three ways in which this can be accomplished. These are shown in figure 5 The arrangement shown in figure 5a gives interatomic distances in better agreement with expectation than do the other two.

TABLE 9

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Reflections observed from (*eeo*) and (*ooe*)

EQUATORIAL ZONE *a*, AXIS OF ROTATION		EQUATORIAL ZONE *b*, AXIS OF ROTATION		EQUATORIAL ZONE *c*, AXIS OF ROTATION	
(021) w.	$(0\bar{2}1)$ m s.	$(20\bar{1})$ w.	(201) v.w.		$(\bar{3}30)$ v.w.
(041) m.	$(0\bar{4}1)$ m.	(401) m.s.	(401) m.w.		$(\bar{1}50)$ w.
(081) m.w.	$(0\ \bar{12}\ 1)$ v.w.	(601) v.w.	$(10\ 0\ 1)$ v.w.	(150) w.	$(\bar{5}50)$ v.w.
$(0\ 16\ 1)$ m.	$(0\ \bar{14}\ 1)$ w.		$(12\ 0\ 1)$ m.w.	(350) v.w.	$(\bar{7}50)$ v.w.
	$(0\ \bar{16}\ 1)$ w	$(00\bar{3})$ v.w.	$(14\ 0\ 1)$ v.w.		$(\bar{9}70)$ v.w.
(003) v.w.	$(0\ \bar{18}\ 1)$ w	(203) w.			$(\bar{3}90)$ v.w.
(063) m.w.		$(60\bar{3})$ m.	$(12\ 0\ 3)$ w.		$(\bar{5}90)$ v.w.
$(0\ 16\ 3)$ m.	$(0\ \bar{10}\ 3)$ v w.	$(12\ 0\ \bar{3})$ w.			$(\bar{9}\ 11\ 0)$ w.
	$(0\ 12\ 3)$ m.				
$(0\ 14\ 5)$ w					

FOURTH LAYER LINE *a*, AXIS OF ROTATION			
$(40\bar{1})$ m s	(401) m.		
$(4\bar{2}1)$ m.s.	$(4\bar{4}1)$ w.		
$(44\bar{1})$ w.	$(4\ \bar{10}\ 1)$ v.w.		
$(46\bar{1})$ w.	$(4\ \bar{12}\ 1)$ w.		
(441) m.s.			

The arrangement of figure 5b will be used as the basis for later drawings, but none of the possibilities must really be considered as excluded. In none of the cases do considerations of distances alone fix the group in its rotation around the *c* axis. In no instance can both the symmetry of the point group $P\bar{1}$ and the complete translations of a face-centered lattice be maintained. The arrangements 5b and 5c will, however, preserve the face centering in the *a* and *b* directions, and that of the sulfur atoms in the *c* direction. They appear somewhat more reasonable for this reason, as well as on account of the arrangements they give oxygen ions around the calcium ions. In any case the calcium ions are equidistant from four oxygen ions of closest approach. Strong electrostatic forces are effective in holding the lattice together in the *c* direction only.

It is somewhat instructive to consider the twinning in crystals of gypsum, anhydrite, and $CaSO_4 \cdot 4CO(NH_2)_2$. In general the composition plane of a twinned crystal is one across which the electrostatic binding forces are great and in which the atoms are brought into approximate juxtaposition by rotation about the twin axis. In gypsum and anhydrite the composition plane and twin plane are the same and contain only sulfate groups or calcium ions, (101) of anhydrite and (100) of gypsum, or sulfate groups and calcium ions, (012) of anhydrite. These are all planes across which the binding forces are relatively great. The twinned crystals of $CaSO_4 \cdot 4CO(NH_2)_2$ thus might be expected, as observed, to have (001) as the composition plane.

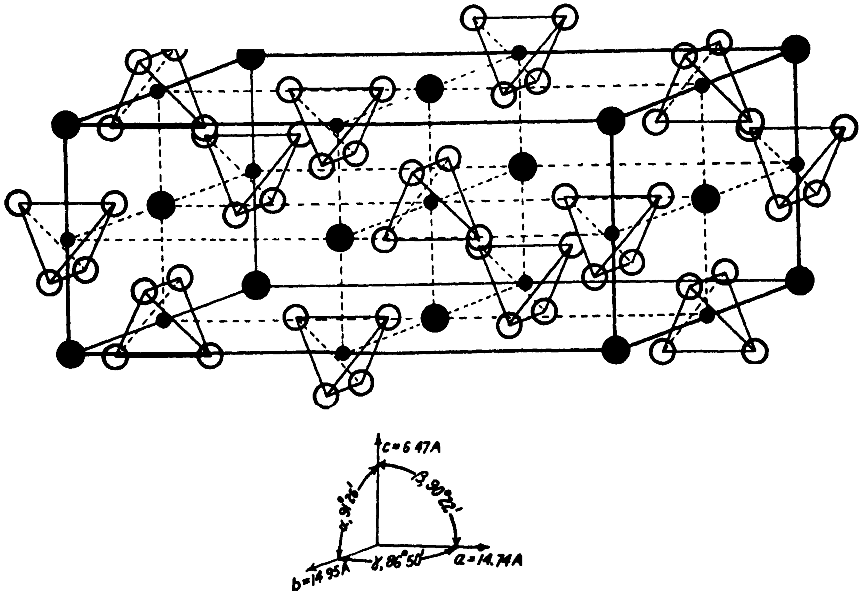

FIG. 6. ARRANGEMENT OF THE Ca^{++} AND SO_4^{--} IONS IN THE UNIT OF STRUCTURE OF $CaSO_4 \cdot 4CO(NH_2)_2$

The birefringence of $CaSO_4 \cdot 4CO(NH_2)_2$, which is almost as great as that of urea, is to be explained by the arrangement of the urea molecules in its structure. These molecules, moreover, must be placed with their oxygen ends near positive charges, calcium ions, and their NH_2 groups near negative ions, the oxygen atoms of the sulfate groups. The lack of prominent cleavage allowed by the calcium sulfate framework is prevented by the urea arrangement. The interatomic distances mentioned in the last section must be satisfied approximately as must also the fundamental face-centered translations.

Since the direction of α does not differ greatly from that of c the planes of urea molecules can not deviate widely from being perpendicular to c. This would also require the obtuse bisectrix and the optic normal to be in (001) with the polarizations along them not greatly different.

A manner, and apparently the only one, of satisfying these manifold requirements is that shown in figures 6 and 7. The undetermined factors in this approximate structure are (1) the exact positions of the sulfate groups and their rotations around the c axis, and (2) the details involved in fixing the positions of the urea molecules, chiefly translations.

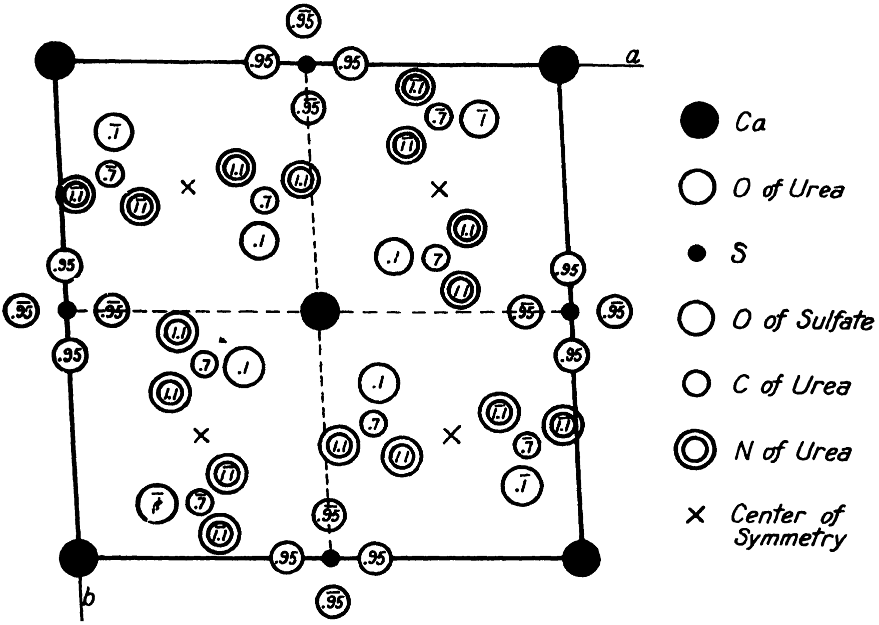

FIG. 7. A PROJECTION OF ONE HALF THE UNIT OF STRUCTURE ON $(001)_0$

The distances of various atoms above and below the plane are shown. The projection on $(001)\frac{1}{2}$ is obtained by translating the origin of this figure to $x = \frac{1}{2}$, $y = 0$. The unit of structure can be formed by the combination of the two projections.

The structure is complete enough to show qualitative agreement between observed and calculated intensities of reflection for simple planes. The various types of absences are accounted for, but of course not in a unique manner. The observed intensities and calculated structure factors for low order reflections from the pinacoids are:

(200) v.s. (020) v.s. $A/4 = F_{Ca} + F_S + 2.9F_{O\text{ of }SO_4} + 1.2F_{O\text{ of }CO(NH_2)_2} - 1.4F_C - 2.8F_N$

(400) s. (040) m.s. $A/4 = F_{Ca} + F_S + 0.7F_{O\text{ of }SO_4} - 3.2F_{O\text{ of }CO(NH_2)_2} + 0.4F_C + 3.2F_N$

(600) a. (060) w. $A/4 = F_{Ca} + F_S - 3.6F_C + 0.7F_N$

(800) m.s. (080) s. $A/4 = F_{Ca} + F_S + 1.6F_{O\text{ of }SO_4} + 1.2F_{O\text{ of }CO(NH_2)_2} + 2.6F_C - 0.6F_N$

(001) a. $A/4 = O$

(002) v.s. $A/4 = F_{Ca} + F_S + 3.9F_{O\text{ of }SO_4} - 1.0F_{O\text{ of }CO(NH_2)_2} + 0.8F_C - 4.0F_N$

(003) v.w. $A/4 = O$

(004) v.w. $A/4 = F_{Ca} + F_S + 3.7F_{O\text{ of }SO_4} - 3.6F_{O\text{ of }CO(NH_2)_2} - 3.8F_C - 3.4F_N$

Moreover it is to be noted that the intensities of *hk*0 for *h* and *k* less than 8 are approximately symmetrical and independent of sign, as would be required by the indicated structure.

CONCLUSIONS

The crystallographic and optical constants of triclinic crystals of $CaSO_4 \cdot 4CO(NH_2)_2$ have been measured. Analysis of x-ray diffraction data led to a partial determination of the crystal structure which is shown in figures 6 and 7.

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REFERENCES

(1) Whittaker, C. W., Lundstrom, F. O., and Hendricks, S. B.: Ind. Eng. Chem. **25**, 1280 (1933).
(2) Schneider, W.: Z. Krist. **69**, 41 (1928).
(3) All structure references, unless otherwise noted, are to Strukturberichte 1913–1928, P. P. Ewald and C. Hermann, Leipzig (1931).
(4) Onorato, E.: Z. Krist. **71**, 277 (1929).
(5) Zachariasen, W. H.: Z. Krist. **80**, 137 (1931).
(6) West, J.: Z. Krist. **74**, 306 (1930).

PHOTOCHEMISTRY OF FLUORESCEIN DYES[1]

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It is well-known that the fluorescein dyes photosensitize the oxidation of readily oxidizable substances by molecular oxygen (Gaffron, 1926; Carter, 1928). Several investigators have shown that peroxide is formed under proper conditions when the dyes are irradiated in solutions which do not contain readily oxidizable substances (Weigert, 1912; Gaffron, 1926; Blum, 1930). The nature of the peroxide has not been clearly shown and the question as to whether it represents an intermediate step in the oxidative process has not been definitely settled. In the following study an attempt has been made to determine the nature of the peroxide formed when fluorescein dyes are irradiated in aqueous solutions (Weigert, 1912; Blum, 1930). Four possible sources for the peroxide have been considered: (1) impurities present introduced in the preparation of the dye, (2) the dye itself, (3) breakdown products of the dye, since the dye is bleached concomitantly with the formation of peroxide, (4) water, resulting in the formation of hydrogen peroxide.

EXPERIMENTAL

The first possibility was tested by preparing fluorescein from very pure intermediates, resorcinol and phthalic anhydride, and purifying carefully by recrystallization. The fluorescein was dissolved by the addition of an equivalent amount of sodium hydroxide, made up to 10^{-3} M and irradiated in a thin layer with a 200-watt tungsten filament lamp at a few centimeters distance. After irradiation for about twenty hours, such solutions contained up to 10^{-3} N hydrogen peroxide, as determined iodometrically. Since the concentration of peroxide formed is of the order of that of the dye, it is highly improbable that it should be a peroxide of any impurities present.

Rate studies

It was thought that simultaneous studies of the rates of bleaching and of peroxide formation should be of value in differentiating between the other three possibilities mentioned above. Such studies offer considerable difficulties, since it is necessary to use fairly intense irradiation over considerable periods of time in order to obtain measurable quantities of peroxide. The method finally adopted was to irradiate successive samples with the same source, a given 200-watt tungsten filament lamp, for varying periods, analysis for peroxide and determination of the degree of bleaching being made for each sample at the end of the irradiation period. Figure 1 is a rate curve obtained in this way. The samples consisted of 100 cc. of a 0.00028 *M* solution of eosin[2] in distilled water, this concentration being selected for convenience in analysis. These samples were placed in a 1000-cc. Erlenmeyer flask, forming a layer approximately 1 cm. thick on the bottom of the flask and supported at a distance of approximately 7 cm. above the filament of an ordinary 200-watt Mazda lamp; the distance between the lamp and the flask was carefully reproduced for each sample. The system was cooled by a blast of air directed across the bottom of the

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[1] This investigation was assisted by a grant from the Board of Research of the University of California.

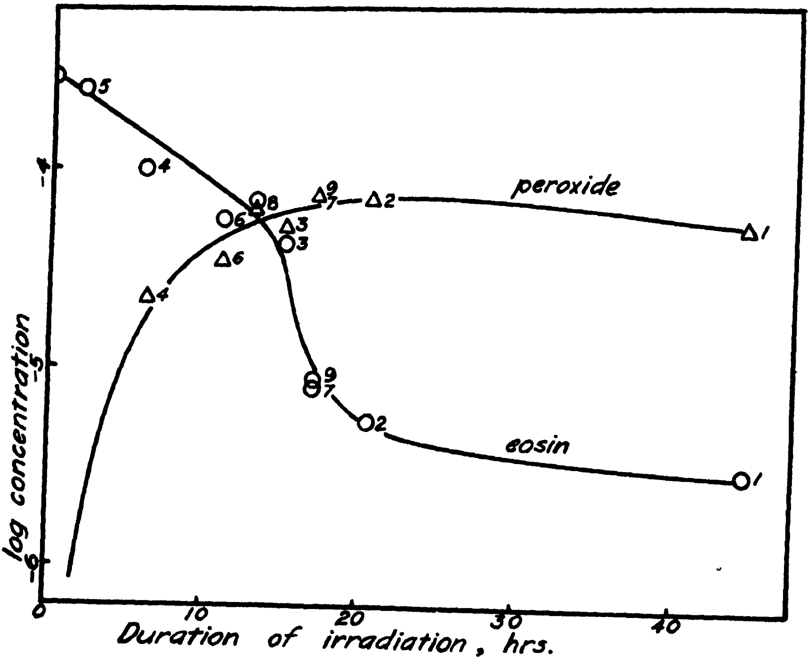

FIG. 1. RATE OF BLEACHING AND PEROXIDE FORMATION FOR IRRADIATED EOSIN

Dye concentrations are in moles per liter; peroxide concentrations in equivalents per liter. Numbers of points indicate the order of the determinations. At 2 hours (point 5) a test for peroxide was obtained, but the quantity was too small for accurate titration.

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[2] Eosin Y (sodium salt of tetrabromofluorescein) from Coleman and Bell.

flask above the lamp bulb; temperatures were maintained in this way between 32°C. and 33°C. after the first half hour of irradiation. The scheme has the advantage that the solution is irradiated in a fairly thin layer, which is of importance since oxygen is a necessary component of the reactions and has a very definite effect on their rate (see Weigert, 1912, and below). Provision for shaking to establish uniform distribution of oxygen was found impracticable because of frothing of the dye solution. It was found difficult to obtain sufficiently intense irradiation for volumes of solution large enough to provide for the removal of aliquots adequate for analysis, and such a method is subject to the objection that the thickness of the layer of solution is altered upon the removal of each aliquot.

The scheme has the disadvantage that the rates are subject to variations in the intensity of emission of the source which definitely varies with the age of the lamp, the extent of this variation being different for different lamps. Some of our determinations were found to be untrustworthy because of this, but the curve shown in figure 1, all the points of which were obtained with the same lamp, seems to be free from this objection. That the intensity of the irradiation did not greatly alter in this case is indicated by the accuracy with which certain of the determinations could be duplicated, and that the points obtained in random order (indicated in the figure) fall on definite curves. Furthermore, the general shape of the dye-concentration curve, i.e., having a sharp break downward at about the time maximum peroxide concentration is reached, was found to be typical of all the curves obtained. The break occurred later with less intense irradiation.

The dye concentrations were determined spectrophotometrically. Although Beer's law does not hold exactly for the fluorescein dyes (see Pringsheim, 1928, p. 226), it was found by determining the absorption of various dilutions of eosin at 5200 A. U., approximately the maximum absorption of eosin, that the law could be applied safely for the concentrations at which our determinations were made. Since some shifting in the absorption spectrum of eosin occurs upon irradiation (see Wood), the absorption spectra of a certain number of irradiated samples were determined; these appear in figure 2. It will be seen from this figure that any shift in the region of maximum absorption is not of great importance in these cases, nor do the curves appear greatly affected by the presence of colored breakdown products. Thus it seems safe to use the absorption at 5200 A U. as an index for calculating the concentration of dye in the irradiated samples; it is probably more correct to consider the concentrations so obtained as maximum dye concentrations, since in the cases of extreme bleaching the presence of breakdown products would probably tend to increase the total absorption.

The photo-compound described by Wood (1922) on the basis of absorption spectrum measurements was studied in the case of fluorescein, but does not appear to play an important part in the reactions herein discussed. It is not formed in the absence of oxygen, but is not a reversible oxidation, since there is no return to the original color when reducing substances are added, hence it is not a peroxide of the dye. It may represent a first step in the oxidative bleaching of the dye. Eosin was used in our rate determinations because the shift in the absorption spectrum is less pronounced than in the case of fluorescein, and therefore the determinations of concentration should be more accurate.

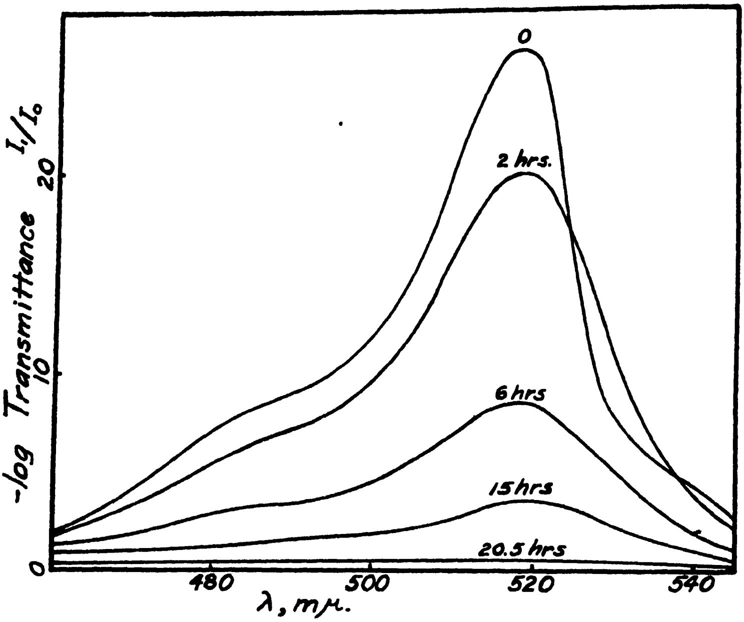

FIG. 2. ABSORPTION SPECTRA OF IRRADIATED 0.00028 M EOSIN

0 non-irradiated dye. Calculations based on absorption of 1 cm. thickness of solution. Higher concentrations diluted 1 to 10 for analysis.

The following method was found satisfactory for the determination of peroxide in the small quantities with which we were dealing. Approximately 2 g. of potassium iodide was placed in a 100-cc. volumetric flask with 5 cc. of 6 N hydrochloric acid and about 70 cc. of water. The sample to be analyzed, usually about 20 cc., was added by pipette and the mixture made up to volume. After standing for 30 minutes, the contents of the flask were emptied into a 500-cc. Erlenmeyer flask and titrated with 0.001 N sodium thiosulfate against starch indicator. The sodium thiosulfate was prepared frequently by dilution from a standardized 0.1 N solution. The end point is sometimes difficult because of the presence of the dye precipitate formed when the acid is added to the dye solution, but the error from this source is not great. The method was checked by titration of solutions of known hydrogen peroxide concentration diluted to the same approximate concentrations as those of our irradiated dye samples, both with and without the addition of non-irradiated dye. The error was estimated as within 5 per cent at the lowest peroxide concentrations at which determinations were attempted; at higher concentrations it was much less. One source of error is the oxidation of iodide ion by atmospheric oxygen, resulting in high values for hydrogen peroxide; this is avoided by keeping the solution in the narrow necked volumetric flask during the 30 minute period before the titration.

The rate curves (figure 1) are subject to certain definite criticisms. Hydrogen-ion concentration was not controlled, because of the fact that electrolytes slow the reaction and hence it was found impracticable to use buffers. The oxygen tension was likewise not controlled for the reasons mentioned above. Both these factors may have an influence on the shape of the rate curves. Nevertheless two facts stand out quite distinctly. After a considerable period of irradiation, the concentration of peroxide may reach a value considerably greater than that of the dye remaining in the solution, e.g., in figure 1 beyond 20 hours the concentration of peroxide is, mole for mole, at least five times as great as the concentration of dye, and thus at least a great part of the peroxide would have to be present in some other form than dye peroxide. The increase of peroxide does not appear to show any direct relationship to the destruction of the dye, indicating that the peroxide is not a compound of breakdown products of the dye.

Behavior of the peroxide

These facts point toward the fourth of the possibilities outlined above, namely, that the peroxide formed upon irradiation of the dyes is hydrogen peroxide. Comparison of the behavior of this peroxide with hydrogen peroxide was therefore made.

Separation of the peroxide from the dye. If the peroxide is hydrogen peroxide it should be possible to separate it from the dye; it was found possible to accomplish this by precipitating the dye as its acid or as an insoluble lake by the addition of Ag^+. When a strong acid (say 0.1 *N* hydrochloric acid) is added to a sample of an irradiated fluorescein dye, the dye is precipitated and can be filtered off. If a filtrate thus prepared was analyzed for peroxide, it was found to contain quantitatively the same amount as a sample from which the dye had not been separated. When the precipitate was redissolved with sodium hydroxide and acidified, no trace of peroxide could be detected.

When silver nitrate is added in excess to an irradiated fluorescein dye solution, the dye is precipitated as an insoluble lake. After centrifuging to throw down the lake, removing the Ag^+ from the decanted solution by the addition of sodium chloride, and filtering, it was found that over 80 per cent of the peroxide appeared in the filtrate, and no trace in the precipitate. Similarly, when a dye solution to which hydrogen peroxide had been added was treated in the same manner, approximately the same percentage of peroxide was recovered in the filtrate. Fluorescein, eosin, phloxin,[3] and erythrosin[4] all gave similar results.

The chromic acid reaction. This test depends upon the formation of the blue perchromic acid, which may be separated from the aqueous solution because of its solubility in ether. The test is subject to certain difficulties which are discussed by Noyes, Bray, and Spear (reference 6, p. 545). The procedure used by us was as follows: 100 cc. of a 0.001 M solution of eosin was irradiated for 15 hours, at the end of which time a 20-cc. sample of the solution was titrated iodometrically for peroxide, a concentration of approximately 0.001 N being found. Five cc. of 6 N nitric acid was added to 50 cc. of this solution. This precipitated the dye, which was filtered off. To the acid filtrate in a 125-cc. Erlenmeyer flask was added 5 cc. of pure ether, forming a layer a few millimeters thick on the surface of the liquid. Two blanks, one consisting of 50 cc. of the unradiated dye solution, and one of 50 cc. of this solution plus 5 cc. of 0.01 N hydrogen peroxide, were prepared in the same way. Four cc. of approximately 0.01 N potassium chromate was added to each of the above mixtures. The irradiated dye and the blank containing hydrogen peroxide showed a distinct decolorization of the yellow chromate ion, when compared with the blank without hydrogen peroxide, with a faint blue color in the ether layer when viewed from the side through the total thickness of the layer. The ether layer in the blank remained colorless. The intensity of the blue color was comparable in the irradiated dye sample and the hydrogen peroxide blank. From this test, we may conclude that the irradiated dye solution, so treated, contained a concentration of hydrogen peroxide approximately the same as that in the blank, namely 0.001 N, which compares favorably with the figure for the iodometric titration.

Rate of reduction by hydrogen iodide. The rate of reduction of our peroxide by hydrogen iodide was studied as follows: Titration of five 20-cc. samples from 100 cc. of 0.001 M irradiated eosin were made at varying intervals after adding 4 cc. of 6 N hydrochloric acid and 4 g. of potassium iodide to each sample. The intervals covered a period of 30 minutes and provide data for a rate curve for the reduction of the peroxide with hydrogen iodide. Sodium thiosulfate (0.001 N) was used for the titration. At the end of 30 minutes the curve had reached a constant value, indicating a peroxide concentration of approximately 0.001 N. Samples of 0.001 N hydrogen peroxide and 0.001 N hydrogen peroxide plus 0.001 M eosin were similarly treated. The rate curves for the three solutions were identical within the limits of accuracy. Since the rate of reduction of the peroxide in the irradiated dye sample is the same as that of hydrogen peroxide, there can be little doubt that the peroxide is the same.

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[3] Dichlorofluorescein.

[4] Tetraiodofluorescein.

Decomposition by catalase. In all the above tests, except the separation of the dye by means of Ag^+, it was necessary to acidify the solution in the course of the procedure, and it is possible that such treatment might bring about the formation of hydrogen peroxide from an existing organic peroxide. The decomposition by catalase was studied in the attempt to avoid this possibility. Catalase is known to decompose hydrogen peroxide at a rapid rate, whereas it does not, so far as has been studied, decompose organic peroxides or peroxyacids at a perceptible rate (Stern, 1932). Catalase was prepared from liver according to the method described by Waksman and Davidson (reference 11, p. 253). When 5 cc. of the catalase mixture was added to 25 cc. of irradiated dye solution containing approximately 10^{-3} N peroxide, the decomposition of the peroxide occurred rapidly at a rate comparable with the decomposition of a similar solution of hydrogen peroxide. When the catalase was inhibited by adding 5 cc. of 10 per cent sodium cyanide to like samples, decomposition of the peroxide did not occur, indicating that the above decomposition was due to the catalase and not to reduction of hydrogen peroxide by reducing substances which might have been present in the catalase mixture.

The above experiments indicate that hydrogen peroxide is formed, and since the quantity bears no direct relation to the quantity of dye or of breakdown products, it is reasonable to assume that it is formed from water and oxygen. The following energy calculations show that this is possible. The principal reaction involved would appear to be:

$$2H_2O\ (l) + O_2 \rightarrow 2H_2O_2\ (aq);\ F_{298} = 50{,}180 \text{ calories};\ H = 46{,}000 \text{ calories}^5 \quad (1)$$

This gives a thermal equilibrium concentration of hydrogen peroxide of about 10^{-18} M (Lewis and Randall, reference 4, pp. 596–7). In agreement with this we found that a dye solution showed no measurable peroxide formation in the dark over a two week's period. On the other hand, the hydrogen peroxide concentrations of the order of 10^{-3} M formed in the light indicate we are dealing with a purely photochemical reaction, and not, for example, a thermal chain reaction initiated by light.

Lacking experimental evidence, no scheme will be offered here for the intermediate steps necessary in the above reaction. It is possible that a

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[5] The data for the calculation of F and H in this paper were obtained from Lewis and Randall (1923). The values of H are taken to the nearest 1000 calories, which is sufficient for our purposes.

dye peroxide may be formed, but if so, it must break down very rapidly to hydrogen peroxide and dye.

The value of 46,000 calories for ΔH is equivalent to a quantum with wave length 6195 A.U.,[6] and this represents the maximum wave length which may bring about this reaction. The absorption spectra of the fluorescein dyes in the visible region are included below this wave length. It is understood that this maximum wave length is only approximate, since some molecules will contain energy greater than the mean value and may be raised to the necessary level by smaller quanta.

The reaction:

$$2H^+ + O_2 = H_2O_2\ (aq);\ \Delta F = -31{,}470 \text{ calories} \tag{5}$$

has a large negative free energy but could not account for the concentration of hydrogen peroxide formed in our experiments, since the concentration of H^+ limits the concentration of hydrogen peroxide which can be formed to 10^{-14} M.

The mechanism:

$$\begin{gathered} D + O_2 = 2O + D;\ \Delta H = 128{,}000 \text{ calories}^7 \\ H_2O + O = H_2O_2 \end{gathered} \tag{6}$$

is, likewise, ruled out since reaction 6 would require 128,000 calories, which represents a maximum wave length of less than 3000 A.U., to which our vessel is opaque.

Some energy of activation would be required to forward reaction 1, and if this were high, the maximum wave length must have a considerably lower value. Unfortunately the data for calculating this energy of activation is not available; it might be greatly reduced by intermediate steps.

The mechanism of bleaching

The bleaching which occurs concomitantly with peroxide formation is not the reduction of the dye to its leuco base, as is shown by the fact that the color does not return when oxidizing agents are added. While this bleaching reaction has been treated as a separate reaction above, we have obtained evidence that it is dependent upon peroxide formation: (1) In the absence of oxygen neither bleaching nor peroxide formation occurs, e.g., a solution of 0.000614 M eosin was irradiated for 5 hours in an evacuated flask, evacuation being carried sufficiently low to boil off some of the water. At the end of the irradiation the volume of solution was found to be 15 per cent reduced owing to the evacuation, its concentration being 0.00074 M eosin. This agrees within the limits of accuracy with a concentration of

[6] See Taylor (reference 9) for calculation.

[7] Value from Mecke (1929).

the dye by a reduction of volume of 15 per cent, i.e., 0.00072 *M*. (2) When a readily oxidizable substance (sodium thiosulfate) is present which may react with the peroxide, bleaching is greatly inhibited, e.g., a sample of 0.0006 *M* eosin was bleached over 99 per cent during 12 hours irradiation, a sample containing the same concentration of dye plus 0.025 *N* sodium thiosulfate was bleached less than 20 per cent during a like period of irradiation. In the latter case sodium thiosulfate was oxidized in quantity corresponding to 0.005 equivalent per liter, a quantity equivalent to approximately four times the peroxide concentration equivalent mole for mole to that of the dye originally present. This indicates that the quantity of peroxide formed has no direct relation to the quantity of dye bleached. These facts indicate that the bleaching is not a direct decomposition of the dye molecule following the absorption of a quantum of energy, as does also the fact (see figure 1) that the rate of bleaching in the absence of oxidizable substance other than the dye, is not a straight line function of the number of molecules present.

As mentioned above, a dye solution remaining in the dark for two weeks formed no peroxide; no bleaching had occurred in the same time. A similar solution containing 10^{-3} *N* hydrogen peroxide likewise showed no bleaching, but a decrease in peroxide concentration comparable to that of a similar hydrogen peroxide solution without dye. Similarly, an irradiated dye solution shows a slow decrease in peroxide concentration if maintained in the dark for some hours after irradiation, but no bleaching of the dye. The behavior of the peroxide in the irradiated dye solution is, thus, similar to that of hydrogen peroxide, i.e., it does not react with the dye in the absence of light.

On the other hand, hydrogen peroxide rapidly bleaches the dye in strongly alkaline solution. This suggested the possibility that the reaction between hydrogen peroxide and dye may be activated by light, and it was found that dye solution containing hydrogen peroxide bleaches much more rapidly in light than does a similar dye solution without hydrogen peroxide, e.g., 0.0006 *M* eosin plus 0.005 *N* hydrogen peroxide bleached 40 per cent in 4 hours; a similar dye solution without hydrogen peroxide bleached only 15 per cent in the same time with the same light source. The activation of the reaction by hydroxyl ion may be considered as due to the reduction of the energy of activation of this reaction; the activation by light as due to the supply of the necessary energy of activation by a light quantum absorbed by the dye molecule. The latter would be more probable than that the hydrogen peroxide molecule is activated by light, since hydrogen peroxide does not absorb appreciably in the spectral region supplied by our light source (Urey et al, 1929). Such a mechanism might readily explain the shape of our rate curve (figure 1). The formation of hydrogen peroxide and the oxidation of the dye by hydrogen peroxide would both be dependent upon the absorbed radiation. The second reaction, being dependent upon the first, would proceed much more rapidly as the hydrogen peroxide concentration was increased, which would account for the S-shaped curve. Such an explanation would also account for the findings of Wood (1922) whose experiments must have been conducted under conditions similar to ours, i.e., without control of hydrogen-ion concentration or oxygen tension. Wood found that a solution of fluorescein bleached more rapidly when a small portion of it was subjected to concentrated radiation, than when the same quantity of radiation was distributed over a larger surface. In the first case the break in the rate curve would occur earlier than in the second. We actually found that the break occurred earlier with more intense radiation; and if taken at the proper time, the solution subjected to the more intense radiation would show the greater bleaching. Wood suggested that his results were due to the fact that each dye molecule must absorb two quanta of energy before the decomposition occurs; this assumption is not necessary to explain the facts if the above scheme is adopted.

Inhibition by oxygen

Weigert (1912) has shown that peroxide formation is inhibited by high partial pressures of oxygen. We have found that when the oxygen tension is raised from 0.2 atmosphere (air) to one atmosphere, peroxide formation and bleaching are both inhibited for a time. The same treatment inhibits the oxidation of a readily oxidizable substance (sodium thiosulfate) when photosensitized by eosin. The nature of this inhibition is not clear and no hypothesis will be offered at the present time.

SUMMARY

1. The peroxide formed when fluorescein dyes are irradiated in aqueous solution is probably hydrogen peroxide.

2. It is suggested that the bleaching of the dyes by light is an oxidation of the dye by the hydrogen peroxide, this reaction requiring activation of the dye molecule by light.

REFERENCES

(1) Blum, H. F.: Biol. Bull. **58**, 224 (1930).
(2) Carter, C. W.: Biochem. J. **22**, 575 (1928).
(3) Gaffron, H.: Biochem. Z. **179**, 157 (1926).
(4) Lewis, G. N., and Randall, M.: Thermodynamics. McGraw-Hill Book Co., New York (1923).
(5) Mecke, R.: Naturwissenschaften **17**, 996 (1929).
(6) Noyes, A. A., Bray, W.,C., and Spear, E. B.: J. Am. Chem. Soc. **30**, 481 (1908). A System of Qualitative Analysis for the Common Elements, III.
(7) Pringsheim, P.: Fluorescenz u. Phosphorescenz. Berlin (1928).
(8) Stern, K. G.: Z. physiol. Chem. **209**, 176 (1932).

(9) Taylor, H. S.: A Treatise on Physical Chemistry. D. Van Nostrand Co., New York (1931).
(10) Urey, H. C., Dawsey, L. H., and Rice, F. O.: J. Am. Chem. Soc. **51**, 1371 (1929).
(11) Waksman, S. A., and Davison, W. C.: Enzymes. Williams & Wilkins Co., Baltimore (1926).
(12) Weigert, F.: Nernst Festschrift, p. 464 (1912).
(13) Wood, R. W.: Phil. Mag. **43**, 757 (1922).

A STUDY OF SEVERAL REACTIONS OF CARBON TETRACHLORIDE SYNTHESIS

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INTRODUCTION

The manufacture of carbon tetrachloride, mainly for use as a grease solvent or as a fire extinguisher, is a relatively important industry. In 1925 the value of the output had reached the million dollar mark. Owing to its advantageous properties, the demand for carbon tetrachloride would undoubtedly increase if its price could be decreased. A glance at current prices shows carbon tetrachloride at about 6 cents per pound in drums and chlorine at below 2 cents in tank cars. There would seem to be much advantage in the discovery of a process of manufacture of carbon tetrachloride superior to the old carbon bisulfide chlorination process now in use.

The whole field of the chemistry of carbon tetrachloride is very dark, and what illuminated spots there are, are quite unattached. As will be recalled, the direct synthesis of carbon tetrachloride has not been successfully carried through, commercially. Theoretically there seems to be no reason why this synthesis does not take place readily. Recently both Bodenstein and Stock have been working on this subject, without obtaining results which were satisfactory either commercially or theoretically. The present study was instituted to investigate this field further and to attempt to help toward the clearing up of the situation.

The principal problems in our carbon tetrachloride research are the difficulty with which carbon tetrachloride forms and the difficulty with which its presence can be detected when at a low partial pressure in related gases. The difficulty of formation might be explained by steric hindrance (1). Practically all of the proposed schemes studied involve one reaction step which cannot at present be carried out practically, regardless of the free energy change. This is usually, but not always, the step in which the carbon tetrachloride is finally produced. Of course, the problem may be merely that of finding the proper catalysts, which no one has definitely discovered in spite of many trials. However, it also has the appearance of something more complicated, possibly the "false equilibrium" which Duhem describes (2) so thoroughly. This phenomenon seems to be found so far in the following reactions, proceeding from either side,

$$\mathrm{C + 2Cl_2 = CCl_4} \tag{1}$$

$$\mathrm{2COCl_2 = (COCl_2)_2} \tag{2}$$

$$\mathrm{2COCl_2 = CO_2 + CCl_4} \tag{3}$$

and probably in

$$\mathrm{C_2Cl_6 + Cl_2 = 2CCl_4} \tag{4}$$

Hood's explanation for the second reaction (3) is that the catalyst was poisoned by phosgene, but he did not investigate the phenomenon further.

Owing to the absence of simple and reliable methods for analysis of the small amounts of carbon tetrachloride that might be obtained in its formation reactions, the decomposition reactions have been studied much more widely, in fact, almost entirely. Arcs, sparks, visible and ultra-violet light, and heat with various catalysts have been some of the means employed. The principal reactions that we will consider are the following; they are gas phase or gas–solid interface reactions.

$$\begin{aligned} \mathrm{C + 2Cl_2} &= \mathrm{CCl_4} \\ \mathrm{C_2Cl_6 + Cl_2} &= \mathrm{C_2Cl_4 + 2Cl_2 = 2CCl_4} \\ \mathrm{2COCl_2} &= \mathrm{CO_2 + CCl_4} \end{aligned}$$

They may all proceed simultaneously, but something has been learned about their catalysts and reaction temperatures, so that each has been studied separately. It is very difficult to study their reaction rates quantitatively, and this has not been attempted by anyone as yet. These three reactions will be considered under separate headings.

In the present research pure and dehydrated chemicals were not used, as it was desired to study conditions that might be commercially obtained. Another item is that stopcocks were never greased, but were well ground and practically gas-tight, and the apparatus was run at slightly over atmospheric pressure. Any thermodynamic data taken from the literature and for which we have not given the source have been obtained from the International Critical Tables (4).

We have been working in what appears to be a very large field. Accordingly, it has not been possible to allow to any of the reactions investigated a sufficient amount of study to carry it to anything like a logical conclusion. However, we plan to continue study of these reactions, particularly the first and third mentioned above.

THE SPECIFIC HEAT OF CARBON TETRACHLORIDE VAPOR

No instance has been found in the literature of the direct determination of the molar specific heat at constant pressure of gaseous carbon tetrachloride. Capstick (4) determined the ratio of the specific heats as 1.13 at 20°C., which, on using Berthelot's relationship (5) for their difference,

$$C_p - C_v = R\left(1 + \frac{27\,pT_c^3}{16\,p_cT^3}\right)$$

yields for the value of C_p, 17.7 calories per mole at 0.1 atmosphere. Applying the correction for pressure, as will be later outlined, to obtain the value at 1 atmosphere, the result is 18.4 calories. Owing to its magnitude with respect to R, C_p calculated from Capstick's data is probably inaccurate. Furthermore, we have no indication of the slope of the relationship between C_p and T. Therefore we decided to calculate C_p for the vapor at 1 atmosphere. For temperatures below the boiling point this condition would be merely hypothetical, but the results just as useful. We employed the following equation, which can be derived exactly by thermodynamics (6):

$$C_p(\mathrm{g}) = C + \frac{\mathrm{d}L}{\mathrm{d}T} - \frac{L}{T} + T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p \frac{\mathrm{d}p}{\mathrm{d}T} + B$$

C is the specific heat of the liquid under its saturated vapor, L is the heat of vaporization under saturation conditions, $\left(\frac{dV}{\mathrm{d}T}\right)_p$ is for the vapor at the saturation pressure, and B is a term to convert C_p from the saturation pressure to 1 atmosphere. The value of B is determined as follows (6):

$$\left(\frac{\mathrm{d}C_p}{\mathrm{d}p}\right)_T = -T\left(\frac{\mathrm{d}^2V}{\mathrm{d}T^2}\right)_p; \; B = T\int_1^p \frac{\mathrm{d}^2V}{\mathrm{d}T^2}\,\mathrm{d}p$$

Since there are insufficient actual experimental data, Berthelot's equation of state was assumed to hold closely enough for the calculation of this correction term. Several simplifications were necessary to avoid tedious computations, involving mainly introduction of the perfect gas law for reduction of the smaller terms. The final result is:

$$B = -\left.\frac{6R^4T^4}{RT(R^3T^3 - ap) + 2abp^2}\right]_1^p$$

where a and b are the Berthelot constants, which in terms of the critical point data are given as

$$a = 16/3\; p_cV_c^2T_c \text{ and } b = V_c/4$$

The value of C was obtained from Hirn's and from Regnault's results (7), and is expressed by

$$C = 30.5 + 0.0209t + 0.000205t^2$$

giving calories per mole in terms of degrees Centigrade. L we obtained from the published data. $\mathrm{d}L/\mathrm{d}T$ we calculated by passing a cubic equation in T through four selected values of L. By differentiation,

$$\frac{\mathrm{d}L}{\mathrm{d}T} = -59.17 + 0.316T - 0.000518T^2$$

To obtain $T(\mathrm{d}V/\mathrm{d}T)_p$, Berthelot's equation in the form

$$pV = RT\left(1 + \frac{9pT_c}{128p_cT}\left(1 - 6\frac{T_c}{T}\right)^2\right)$$

is differentiated, giving as the desired quantity

$$T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p = \frac{RT}{p} + \frac{108RT_c^3}{128p_cT^2} = 0.082\left(\frac{T}{p} + \frac{3{,}245{,}200}{T^2}\right)$$

This quantity is in liters, for p in atmospheres. Owing to the complexity of the $p - T$ relationship as shown by the data of Young (4), $\mathrm{d}p/\mathrm{d}T$ was not obtained directly, but was calculated by the Clapeyron-Clausius equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_g - V_l)} = \frac{0.26794L/T}{\dfrac{1}{d_g} - \dfrac{1}{d_l}}$$

in atmospheres per degree Centigrade for carbon tetrachloride. The figures calculated by this equation agree very well with differences from Young's data. His density data were used. For the point at 20°C. the empirical equation, to be discussed later, was employed:

$$\log p_{\mathrm{mm.}} = 7.8717 - \frac{1732}{T}$$

C_p was calculated up to 280°C., although it was expected that at the higher temperatures it might be unreliable. The critical temperature is 283°C. The results of the calculations are shown in table 1. The values of C_p have been plotted in figure 1. The straight line curve which we have drawn through the points appears to us to be the most probable locus of the true values. Its equation is:

$$C_p = 14.0 + 0.0233T$$

Certainly the accuracy cannot be high, owing mainly to uncertainties in dL/dT, C, and $(dV/dT)_p$, particularly at the two or three temperatures, but the graph is a useful indication, and is probably not in error by more than 2 calories between 0°C. and 300°C. From the graph we find $C_{p,298}$ = 20.9.

TABLE 1

Calculation of C_p of carbon tetrachloride(g) at 1 atmosphere

t	dp/dT	$T\left(\frac{dV}{dT}\right)_p$	$-L/T$	dL/dT	$T\left(\frac{dV}{dT}\right)_p \frac{dp}{dT}$	C	B	$C_p(g)$
degrees C	*atmospheres per degree C*	*liters*	*calories per degree C*	*calories per degree C*	*calories per degree C*	*calories per degree C*	*calories per degree C*	*calories per degree C*
20	0 00557	196 6	−26 52	−11 07	26 70	30 97	0 68	20 8
80	0 03301	28 38	−20 12	−12 17	22 72	33 46	−0 04	23 9
120	0 0734	11 97	−16 53	−15 01	21 35	35 92	−0 71	25 0
160	0 1360	6 30	−13 53	−19 46	20 80	39 06	−1 64	25 2
200	0 2255	3 89	−10 64	−25 60	21 30	42 83	−2 86	25 0
240	0 351	2 64	−6 69	−33 42	22 50	47 30	−4 33	25 4
280	0 530	1 92	−2 91	−42 85	24 70	53 05	−6 34	25 6

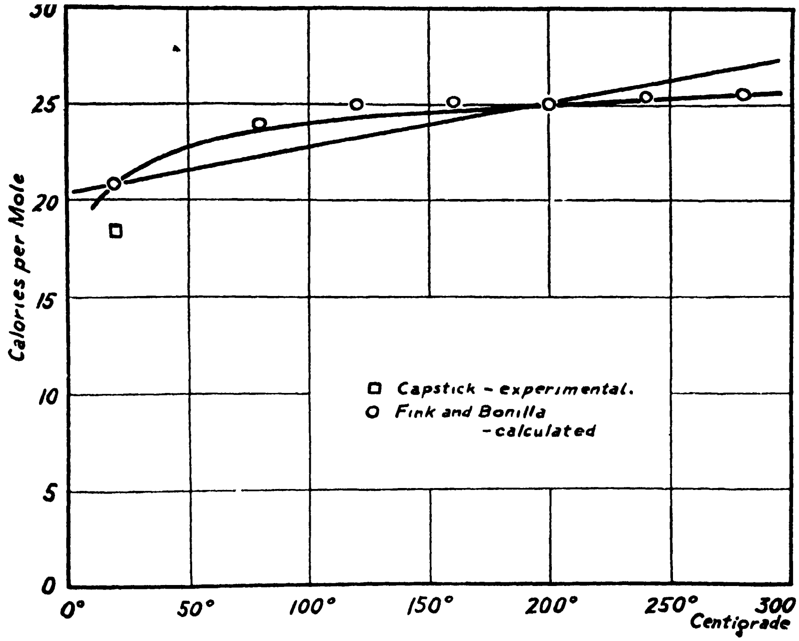

Fig. 1 C_p of Carbon Tetrachloride Vapor at 1 Atmosphere

If it is desired to fit an equation more closely to the calculated points, the following one may be used, which, plotted, gives the curve in figure 1, probably preferable for extrapolating:

$$C_p = 21.6 + 0.0073T - 1.4 \times 10^{25}\ T^{-10}$$

THERMODYNAMIC DATA FOR THE SUBSTANCES INVOLVED

C (graphite):

$C_p = -1.652 + 0.01676T - 0.00001727T^2 + 0.0^{8}994T^3 - 0.0^{11}263T^4$.

$C_{p,\,298}$ = 2.05 calories per mole degree.

S_{298} = 1.3 calories per mole degree.

$C_p = 6.4 - 26{,}500/T^{3/2}$ (approximate, Fink and Bonilla).

Cl_2(g):

$C_p = 7.4 + 0.001T$; $C_{p,\,298} = 7.7$.

S_{298} = 26.62 calories per atom degree.

CCl_4:

$\Delta H_{293}(g) = -25{,}430$ calories per mole.

$\Delta H_{298}(g) = -25{,}430 + 5(20.9 - 15.4 - 2.05) = -25{,}410$.

$S_{298}(l) = 49.06$.

$\Delta S_{298}(l)$ of $CCl_4 = 49.06 - 4 \times 26.62 - 1.3 = -58.72$.

ΔH_{298} (vaporization) = 7,700; p_{298} = 114.7 mm.

$\Delta H_{298}(l) = -25{,}410 - 7{,}700 = -33{,}110$.

$\Delta F^\circ_{298}(l) = -33{,}110 + 298 \times 58.72 = -15{,}610$.

$\Delta F^\circ_{298}(g) = -15{,}610 - RT(\ln 114.7 - \ln 760) = -14{,}490$ calories per mole at 1 atmosphere.

$C_p = 14.0 + 0.0233T$; $C_{p,298} = 20.9$.

$COCl_2$:

$\Delta H_{298}(g) = -51{,}920$; $\Delta F^\circ_{298}(g) = -48{,}960$ (8).

p_{298} = 1500 mm.

$\Delta F^\circ_{298}(l) = -48{,}960 - RT(\ln 760 - \ln 1500) = -49{,}370$.

$C_{p,298}(g) = 13.3$ (by interpolation; see later).

CO_2(g) (9):

$\Delta H = -94{,}210 - 0.30T + 0.003T^2 - 0.0^{6}1T^3$; $\Delta H_{298} = -94{,}280$.

$\Delta F = -94{,}210 + 0.30\ T \ln T - 0.003T^2 + 0.0^{7}5T^3 - 0.94T$.

$\Delta F^\circ_{298} = -94{,}010$.

$C_p = 7.40 + 0.0066T - 0.0000015T^2$.

$SiCl_4$:

$\Delta H_{298}(g) = -142{,}650$; $\Delta H_{298}(l) = -149{,}100$.

$S_{298}(l) = 56.43$; p_{298} = 234.5 mm.

ΔS_{298} (formation) $= 56.43 - 4 \times 26.62 - 4.54 = -54.59$.

$\Delta F^\circ_{298}(l) = -149{,}100 + 298 \times 54.59 = -132{,}800$.

$\Delta F^\circ_{298}(g,\ 1\ \text{atmosphere}) = -132{,}800 - RT \ln\dfrac{234.5}{760} = -132{,}100$.

$C_{p,298}(g) = 20.9$ (1 atmosphere; assumed equal to CCl_4).

$SnCl_4$:

$\Delta H_{298}(g) = -118{,}300$; $\Delta H_{298}(l) = -127{,}360$.

$S_{298}(l) = 61.84$; p_{298} = 24.02 mm.

$\Delta S_{298}(l)$ (formation) $= 61.84 - 4 \times 26.62 - 12.50 = -57.14$.

$\Delta F^\circ_{298}(l) = -127{,}360 + 57.14 \times 298 = -110{,}420$.

$\Delta F^\circ_{298}(g) = -110{,}420 - RT \ln\dfrac{24.02}{760} = -108{,}300$.

$C_{p,298}(g,\ 1\ \text{atmosphere}) = 20.9$.

$AlCl_3$

$\Delta H_{298}(s) = -167{,}000$, $\Delta H_{298}(g, 1\ \text{atmosphere}) = -140{,}620$ (10)

$S_{298}(s) = \frac{3}{2}R \ln 26\ 97 \times 35\ 455^3 - 3\ 76 = 37\ 97$ (see later)

$\Delta S_{298}(s)$ (formation) $= 37\ 97 - 3 \times 26\ 62 - 6\ 73 = -48\ 62$

$\Delta F^\circ_{298}(s) = -167{,}000 + 298 \times 48\ 62 = -152{,}510$

$p_{298} = 0\ 00025$ mm (10), $C_p(s) = 6n = 24$ (assumed for 298)

$\Delta F^\circ_{298}(g, 1\ \text{atmosphere}) = -152{,}510 - RT \ln \frac{0\ 00025}{760} = -143{,}660$

SiO_2 (quartz)

$\Delta H_{298} = -202{,}000$ (4, 11), $S_{298} = 9\ 81$ (see later)

$\Delta S_{298} = 9\ 81 - 4\ 54 - 2 \times 24\ 52 = -43\ 77$, $C_p = 10\ 7$

$\Delta F^\circ_{298} = -202\ 000 + 298 \times 43\ 77 = -188\ 960$

SnO_2 (amorphous)

$\Delta H_{298} = -137{,}800$, $\Delta F^\circ_{298} = -123{,}200$ (12), $C_p = 13\ 5$

Al_2O_3 (amorphous)

$\Delta H_{298} = -384{,}000$ (11), $\Delta F^\circ_{298} = -356{,}600$, $C_p = 19\ 01$

When not otherwise indicated the source of data in this table is the International Critical Tables (4)

No data were found on the specific heat of phosgene gas We will assume that the variation of $C_p(g)$ along the series methane methyl chloride methylene chloride–chloroform–carbon tetrachloride should be quite similar to that for the series carbon dioxide phosgene carbon tetrachloride, as would be expected to be approximately true Since, furthermore, the values of $C_{p\ 298}$ are almost equal for carbon dioxide and for methane, those for phosgene and for methylene chloride should similarly be equal C_p for the latter compound, however, was not available in the literature, and has therefore been obtained by interpolation, in figure 2 The result is 13 3

No data were found on S for aluminum chloride or any similar compounds, so Latimer's approximation was used, since aluminum has at 298°C almost reached the Dulong and Petit value

Although sufficient C_p data are available, the entropy of quartz has apparently not been calculated This we have done graphically, using the well-known relationship

$$S_T = \int_0^T \frac{C_p}{T}\,dT$$

The graphical integration gives 9 81 as the entropy of quartz at 298°C

THE CHLORINATION OF C_2Cl_4 AND OF C_2Cl_6

One of the reactions of which the reverse is found to occur in several of the methods of decomposition of carbon tetrachloride is

$$C_2Cl_4 + 2Cl_2 = 2CCl_4$$

Lob (13) has shown it to occur in the action of a hot platinum filament on carbon tetrachloride vapor The only study of the thermal reaction has been that due to Weiser and Wightman (13), also on the decomposition of carbon tetrachloride, and very much from a practical point of view. Some fairly helpful results can be calculated from their data if the assumption is made that they approached the equilibrium, which seems likely. However, it must be remembered that this may not be the theoretical

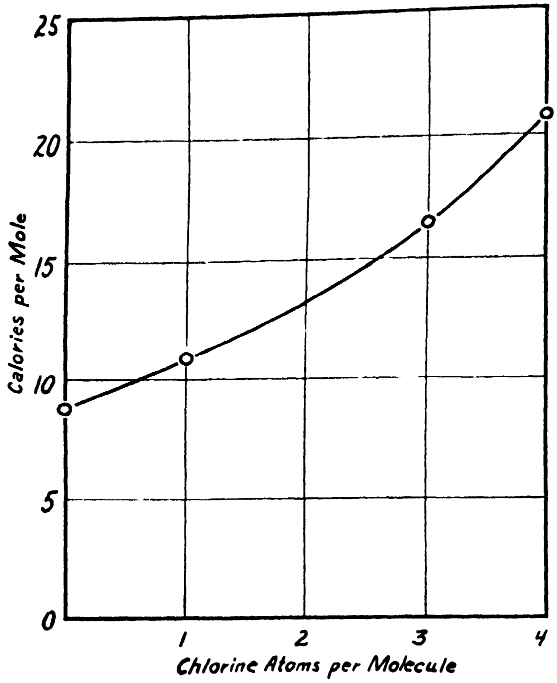

FIG. 2. C_p AT 298° K. AND 1 ATMOSPHERE FOR THE GASES CARBON DIOXIDE, METHANE, METHYL CHLORIDE, CHLOROFORM, AND CARBON TETRACHLORIDE

TABLE 2

The reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$

(Calculated from Weiser and Wightman)

t (CORRECTED)	$1/T$	C_2Cl_4	CCl_4	Cl_2	TOTAL MOLES	TOTAL VOLUME	$\log_{10}K$	K_p	$\Delta F°$	ΔH
degrees C.		*moles*	*moles*	*moles*		*liters*				
750	0.000980	0.219	0.581	0.442	1.242	104	−2.91	0.00122	13,600	
850	0.000883	0.278	0.451	0.566	1.295	119	−2.42	0.00378	12,400	
900	0.000855	0.238	0.516	0.493	1.247	120	−2.74	0.00182	14,700	15,000
1025	0.000769	0.278	0.454	0.564	1.296	138	−2.51	0.00310	14,900	
1125	0.000714	0.351	0.297	0.572	1.220	140	−2.032	0.00928	13,000	

The number of moles given here is that obtained for a constant amount of carbon tetrachloride passed through the tube.

equilibrium; this will be discussed later. Weiser and Wightman's temperatures are for no gas flow, which we have approximately corrected to actual gas temperatures from data supplied by them. A further correction was made: the carbon tetrachloride unaccounted for was portioned up between CCl_4 and C_2Cl_4 in ratio of the two vapor pressures, using Duhring's rule. Table 2 shows our calculated results. The values for log K were plotted against $1/T$ in figure 3, and $\Delta H'$ obtained from the slope. The only check on these figures is given by Berthelot's incomplete heat of combustion data (14) from which we may say that ΔH of formation of $C_2Cl_4(g)$ will be greater than about −40,000 calories, so that ΔH for the decomposition of two moles of CCl_4 to C_2Cl_4 will be greater than 10,000 calories, compared with 15,000, the value from table 2. Therefore the chlorination of C_2Cl_4 to CCl_4 is thermodynamically quite possible, yet has never been accomplished empirically.

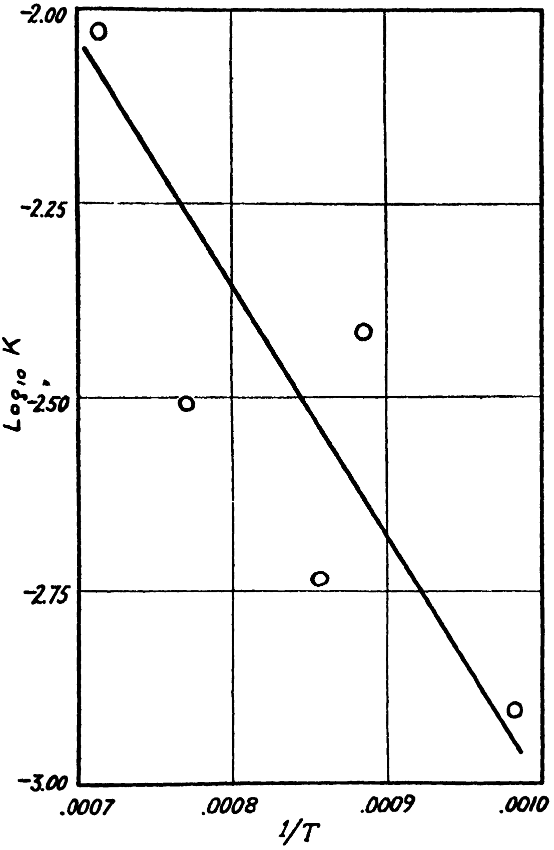

FIG. 3. EXTENT OF THE REACTION $C_2Cl_4 + 2Cl_2 \rightleftharpoons 2CCl_4$

Weiser and Wightman found the gas reaction,

$$C_2Cl_4 + Cl_2 = C_2Cl_6$$

to occur, but at a slower rate than the C_2Cl_4 formation between the temperature limits they used. At lower temperatures the velocity does not decrease as rapidly as may be expected, and it is appreciable at room temperature. Recently (15) the reaction in solution, as affected by light, has also been studied. Berthelot's figures on this reaction (16) are doubtless more accurate than his single heats of combustion, since the errors will cancel to some extent. His data give −54,000 calories for the heat absorbed at room temperature. From these two reactions we obtain the rough value of ΔH, 39,000 for

$$C_2Cl_6(g) + Cl_2 = 2CCl_4(g)$$

which is therefore endothermic, and favored by a temperature rise. This reaction, too, has never been directly carried out. The reverse action, however, has, and as early as 1839 Regnault (17) obtained C_2Cl_6 besides other substances in the following sequence with rising temperatures: C_2Cl_6, C_2Cl_4, C_2Cl_2, C_6Cl_6, C.

Except for carbon tetrachloride, the other carbon chlorides mentioned can all be produced consistently by the action of chlorine on carbon in a heated tube or in a carbon arc, as our own experiments and those of others have shown. Bolton (18), for instance, obtained C_2Cl_6 and C_6Cl_6 in an arc.

From these considerations it is seen that the splitting and chlorination of the inter-carbon bond in C_2Cl_4 and in C_2Cl_6 is the operation which has not been directly carried out so far. The problem seems to reduce itself to finding catalysts for these chlorinations, exothermic and endothermic, respectively, which will not simultaneously assist the decomposition to carbon and chlorine of the carbon tetrachloride formed.

Experimental

In an effort to duplicate Bolton's results and to determine simultaneously whether under any ordinary conditions carbon tetrachloride was produced, we constructed a Pyrex reaction chamber containing two axially perforated electrodes of carbon. The arc was run under varying conditions of length, current, and chlorine flow rate, and the gas was admitted through both carbons. Alternating current was used as well as direct. Another apparatus was constructed, containing a graphite rod heated electrically to the desired temperature in a stream of chlorine. In both of these setups mixtures of solid carbon chlorides, probably C_2Cl_6 and C_6Cl_6, were obtained on the walls and in the exit gas water condenser, but no carbon tetrachloride was obtained. Soaking the electrodes and rods in solutions of metal salts (copper, iron, and nickel) did not seem to make any difference. In the analysis for carbon tetrachloride the issuing gases were all completely condensed in a test tube by means of liquid air. This test tube was then transferred to a beaker containing an ice–salt mixture.

The gas boiling off came out through the tube previously used as inlet, which was of small bore, about 20 cm. long, and for this last operation it was thermally insulated from convection currents by means of a larger concentric tube. By regulating the amounts of salt and ice we found that the desired rate of heating up could be obtained. With this simplified column it was found possible to detect easily about 0.1 cc. of carbon tetrachloride in several cubic centimeters of liquid chlorine.

THE CHLORINATION OF PHOSGENE

A great deal of work has been done by others on the chlorination of metal oxides by chlorine, by phosgene, or by mixtures of carbon monoxide and chlorine, and by carbon and chlorine, on a laboratory scale, at least. All of the oxides tried have been successfully chlorinated, so that it is safe to assume, in general, that any metal chloride can be readily produced by means of cheap chlorinating agents. Silicon dioxide is the most refractory oxide, and when treated with chlorine only, the temperature must approximate 1000°C. before appreciable interaction sets in. It is the only common oxide or anhydride that cannot be chlorinated by phosgene below 600°C.

Chlorinations can also be readily carried out by means of carbon tetrachloride vapor (19, 20), and we felt that some of these latter reactions might be reversed under attainable conditions, particularly the reaction involving silicon dioxide. Three of these reactions were studied by us, experimentally and theoretically. The free energy changes calculated for the reactions show why chlorination by carbon tetrachloride is so successful.

Pyrex glass bomb tubes were dried by heating overnight to more than 600°C. with a slow stream of carbon dioxide dried over magnesium perchlorate, $Mg(ClO_4)_2$, passing continually through the bombs. We then placed the bombs in an ice–salt freezing mixture and passed in and condensed the phosgene and added the metal chloride by means of a special funnel to prevent wetting the stem. Otherwise good seals were difficult. The bombs were then heated for a day at a time to successively higher temperatures. Before raising the temperature each time, the bombs were cooled and inspected for the production of any solid oxides. The following reactions were studied:

Reaction I

$$2COCl_2(g) + SiCl_4(g) = 2CCl_4(g) + SiO_2$$

Approximately a dozen bombs were prepared with up to 4 cc. of each reactant as a liquid, in a total volume of 12 to 15 cc. Several were exposed for days to sunlight, others to a mercury vapor arc, and all were heated to temperatures ranging up to 540°C. Two withstood this temperature and the large pressure involved without bursting. Traces of other chlorides, ferric chloride and aluminum chloride, had been added to two of the bombs to test for any catalytic action. In practically none of these tubes was there found any silicon dioxide deposited on the walls, or any other indication of reaction. Under the mercury arc a rather dense cloud always formed which would later disappear in a few hours or a day, even with the bomb at below 0°C. Quickly breaking the bomb after an exposure to the arc left only the merest amount of powder after the evaporation of the liquids. No corrosion of the glass by the phosgene was noticed, though some investigators (21) have been troubled by such an action on other types of glass.

Reactions II and III

$$3COCl_2(g) + 2AlCl_3(g) = 3CCl_4(g) + Al_2O_3$$
$$2COCl_2(g) + SnCl_4(g) = 2CCl_4(g) + SnO_2$$

Two bombs with aluminum chloride and two with stannic chloride were prepared and treated similarly to those with silicon tetrachloride. Aluminum chloride was used because of its ready availability and stannic chloride because of its similarity to carbon tetrachloride. None of these bombs showed the formation of any oxide, which could have formed according to the above reactions. Even with C_2Cl_6 as an end product no oxides were formed; this reaction should have a greater tendency to occur, as we have already indicated.

Free energy calculations suggest the non-occurrence of the reactions to be due to lack of tendency toward the change rather than to lack of a catalyst. Calculations for 25°C. give the following results:

Reaction I (SiO_2): $\Delta F^\circ = +12{,}080$; $\Delta H = -6{,}370$; $\Delta C_p = +9\ 6$
Reaction II (Al_2O_3): $\Delta F^\circ = +43{,}000$; $\Delta H = +3{,}100$; $\Delta C_p = +7\ 8$
Reaction III (SnO_2): $\Delta F^\circ = +56{,}100$; $\Delta H = +33{,}500$; $\Delta C_p = +5\ 0$

Because of the magnitude of the free energy change, reactions II and III are seen to be hopeless, but reaction I merits a little study. If the three chlorine-containing compounds are in their liquid forms, ΔF° becomes +11,360. The effect of increases in temperature and pressure were approximately calculated, assuming ΔC_p to remain constant over the range.

$$\left(\frac{dF}{dT}\right)_p = -S = -\int \frac{C_p}{T}\,dT = -C_p \ln T + A$$

$$\Delta F_{T_2} - \Delta F_{T_1} = -\int_{T_1}^{T_2} (C_p \ln T + A)\,dT = \left(-C_pT \ln T + (1 - A)T\right)\Big]_{T_1}^{T_2}$$

ΔF° can be calculated closely enough for our purposes by knowing ΔH and assuming ΔC_p constant down to absolute zero. Knowing now ΔF° at two different temperatures, the value of $(1 - A)$, Lewis and Randall's I, can be calculated and

$$\Delta F^\circ_T = -7860 - 5\,T \ln T + 95.1T$$

Thus ΔF° rapidly increases with temperature, decreasing the reaction tendency. For a pressure change

$$\Delta F_{p_a} = \Delta F^0_1 - RT \ln \frac{a^2_{CCl_4}}{a^2_{COCl_2}\, x a_{SiCl_4}}$$

where, approximately,

$$RT \ln a = \int_1^p V \mathrm{d}p$$

for each substance. There is practically nothing in the literature on the gaseous molar volumes (or densities) of the substances involved, so only a rough calculation assuming $a = p$, or, in general, that the activity coefficients cancel, can be carried out. For the greatest yield with a given total pressure P of phosgene and silicon tetrachloride, the pressure of phosgene should be $2P/3$, as can be shown by setting

$$M = p^2_{COCl_2}\, x p_{SiCl_4};\ p_{COCl_2} + p_{SiCl_4} = P$$

and making $\mathrm{d}M/\mathrm{d}p_{COCl_2}$ equal to zero. A final pressure of carbon tetrachloride of 1 atmosphere will be assumed, which in the bombs would have amounted to a deposit of silicon dioxide of about 25 mg. Therefore at a given temperature

$$\Delta F = RT \ln \tfrac{1}{2} p^3_{COCl_2}$$

and at 230°C., just above the critical temperatures of the substances involved, p_{COCl_2} amounts to 3700 atmospheres. The pressure actually would exceed this value, as can be seen from Dodge's reduced pressure versus compressibility curves (22). For the reaction between the liquids rather than the gases, and at 25°C., p is obtained as 740 atmospheres, so that if the reaction velocity is appreciable it would not be impossible to carry out the reaction under these conditions, but probably not commercially in spite of the small work of compression of the liquids.

The effect of the ultra-violet light from the mercury vapor arc lamp was obviously not merely catalytic, as the reaction reversed on removal of the light source, but the light also shifted the equilibrium. This is therefore another action that might be utilized.

THE DIRECT CHLORINATION OF CARBON

Our previously mentioned attempts to carry out the direct chlorination of carbon by chlorine to form carbon tetrachloride indicated that a catalyst was necessary. The reaction is decidedly exothermic and ΔF° of formation under standard conditions of gaseous carbon tetrachloride at 25°C. is $-14{,}500$.

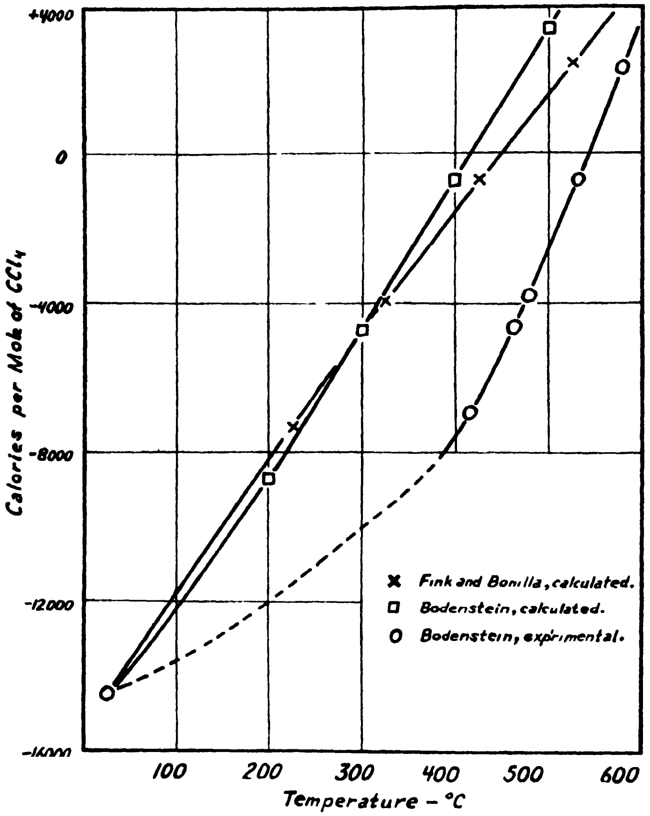

FIG. 4. EXTENT OF THE REACTION $CCl_4 \rightleftarrows C + 2Cl_2$

After many fruitless attempts to find a catalyst, it was decided to attempt to reach equilibrium from the carbon tetrachloride side of the reaction:

$$C + 2Cl_2 = CCl_4$$

At this time Bodenstein's (23) work along this line appeared. His results are plotted in figure 4. They show that it is probably necessary to work at a temperature not over about 500°C. in order to synthesize carbon tetrachloride. Needless to say, this equilibrium was reached by Bodenstein from only one side, and is not very near the thermodynamic or calculated equilibrium. The values for the curves, calculated from Bodenstein's data, are given in table 3. The Nernst heat theorem values (24) have also been plotted, though they involve the rough "chemical constants." We find by using the simpler relationship for $C_p(g)$ of carbon tetrachloride already obtained, and for carbon, the simpler of the expressions given:

$$\Delta H_T = \Delta H_0 + \Delta C_p dT = 21{,}160 + 7.2T - 0.01065T^2 + \frac{53{,}000}{T^{1/2}}$$

TABLE 3

Extent of the reaction $CCl_4 = C + 2Cl_2$

(Calculated from Bodenstein's results)

TEMPERATURE	CARBON TETRACHLORIDE DECOMPOSITION	$-\log_{10}K_p$	CHLORINE FRACTIONAL PRESSURE	$\Delta F°$
degrees C	*per cent*			*calories per mole*
298	—	—	—	14490
417	4 06	2 18	0 078	6900
462	10 0	1 38	0 182	4650
477	13 9	1 10	0 244	3780
530	36 5	0 20	0 535	735
580	66 7	−0 506	0 800	−1790

on substituting the known value of ΔH_{298}. Since $\Delta F°_{298}$ is also known, the general free energy expression is obtained:

$$\Delta F°_T = 21{,}160 - 16\ 6T \log T + 0\ 01065T^2 + \frac{35{,}300}{T^{3/2}} + 8.66T$$

These signs of ΔH and ΔF are for the decomposition of carbon tetrachloride. Values of equilibrium partial pressure of chlorine for 1 atmosphere total pressure were plotted in figure 5. The results of the calculations are shown in table 4. The agreement with the rough heat theorem values is seen from the curve to be fairly close.

Stock (24) has recently succeeded in producing some carbon tetrachloride by the action of chlorine on activated charcoal between 400°C. and 600°C at pressures between 1 and 4 atmospheres. His results were not very reproducible, but interesting. The maximum pressure of carbon tetrachloride that he obtained was at 400°C. and 4.1 atmospheres total pressure, and amounted to 0.29 atmosphere, certainly quite sizeable. Assuming the gas pressure quotient to hold constant over the pressure range, we can

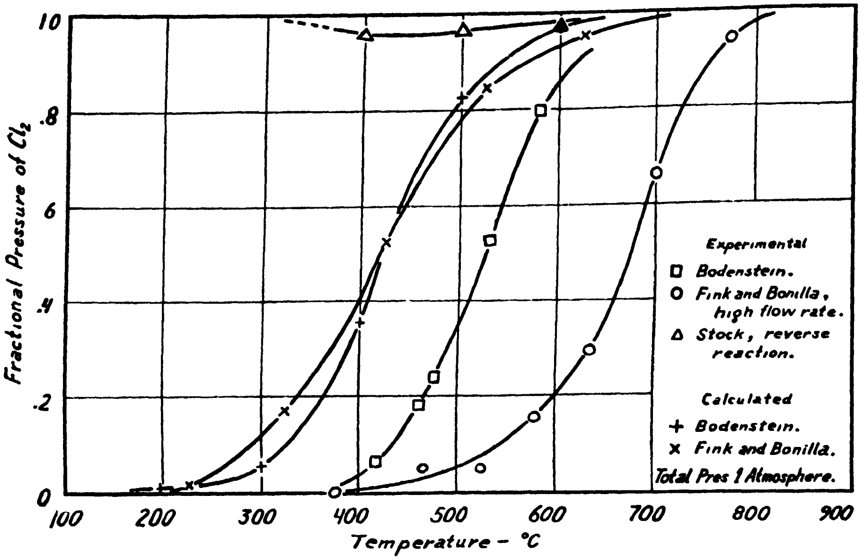

FIG 5 FREE ENERGY CHANGE OF THE REACTION $C + 2Cl_2 \rightleftharpoons CCl_4$

TABLE 4

Theoretical extent of the reaction $CCl_4 = C + 2Cl_2$

TEMPERATURE	$\Delta F°$	$-\log_{10}K_p$	K_p	CHLORINE FRACTIONAL PRESSURE
Absolute	*calories per mole*			
500	7342	3 20	0 00063	0 0248
600	3955	1 437	0 0364	0 1735
700	725	0 226	0 594	0 529
800	−2426	0 661	4 58	0 846
900	−5359	−1 300	19 95	0 954

TABLE 5

The reaction $C + 2Cl_2 = CCl_4$

(Calculated from Stock's experiments)

TEMPERATURE	TOTAL BOMB PRESSURE	PARTIAL CHLORINE PRESSURE	PARTIAL CARBON TETRACHLORIDE PRESSURE	PRESSURE QUOTIENT K_p	PARTIAL CARBON TETRACHLORIDE PRESSURE AT 1 ATMOSPHERE TOTAL PRESSURE
degrees C	*atmospheres*	*atmospheres*	*atmospheres*		*atmospheres*
400	2 5	2 12	0 204	0 0453	0 0416
500	1 65	1 56	0 088	0 0365	0 034
600	1 65	1 58	0 065	0 027	0 0256

calculate that the partial pressure of carbon tetrachloride will equal that of chlorine at a total pressure of about 40 atmospheres. Stock's maximum yields of carbon tetrachloride do seem to indicate a limit of reaction. We have made the appropriate calculations from them, and give the results in table 5. These values we have also plotted in figure 5, and the combination of theoretical and experimental curves for the equilibrium is strikingly similar to the curves given by Duhem (2).

Experimental

We decided to use the decomposition reaction to find a catalyst for the reaction of synthesis, knowing that the same catalyst should theoretically catalyze both opposing reactions. An apparatus was set up in which carbon tetrachloride vapor was produced by boiling the liquid in a graduated flask. The vapor passed through a Pyrex combustion tube in an electric heater. The tube contained a thermocouple hot junction, and in it were placed in different runs the various materials to be tested for catalytic effect. The gases next traversed a gas sampling tube maintained at about 80°C. to prevent condensation of the carbon tetrachloride, and from there were removed by a water jet suction pump in which the pressure was regulated by an air admission valve. A run was ended when the conditions of temperature and flow rate had remained constant for about 30 minutes, which corresponds to a large volume of carbon tetrachloride vapor, as the average flow rate was about 2 cc. of liquid carbon tetrachloride per minute. An excess of strong potassium iodide solution was admitted to the sampling tube, the liquid shaken about, poured out, the tube rinsed with alcohol, and solution and rinsings titrated with standard sodium thiosulfate solution and starch indicator, for free iodine. The partial pressure of chlorine was calculated, knowing the volume of the sampling tube (300 cc.) and the temperature at which it had been held. The carbon tetrachloride pressure was obtained by difference, for which purpose a manometer was connected to the system.

In order to obtain correct results with the above scheme it is necessary that chlorine and carbon should be the only decomposition products of the carbon tetrachloride. With some of the substances tested as catalysts solid and liquid products such as C_2Cl_6, C_2Cl_4, C_6Cl_6, etc., were produced in varying quantities. Many wood charcoals and silicon dioxide were among this class of substances. Ordinary granulated animal charcoal of 88 per cent ash was the best catalyst for the total decomposition, even when present in only small amounts, and no liquid or solid products of carbon tetrachloride decomposition ever condensed when the animal charcoal was used. Runs were made between 300°C. and 800°C. The results have been plotted alongside Bodenstein's curve in figure 4. The total time that the carbon tetrachloride vapor remained in the heated portion of the tube we calculate to have been about 2 seconds, excluding the adsorption by the charcoal. Furthermore, at this high flow rate it is probable that the vapor did not reach the temperature indicated, as the charcoal was never packed tightly and the granules were coarse. The animal charcoal was therefore a very effective catalyst for this reaction, and undoubtedly more active than the charcoal Bodenstein used, though it is difficult to determine how much his reaction rates were affected by diffusion velocity. When chlorine was passed through the heated tube at various temperatures and rates, there was, however, no noticeable carbon tetrachloride formation, using the same system of freezing and redistilling the outcoming gases as previously described under the C_2Cl_4 and C_2Cl_6 reactions.

Since pressure aids the formation of carbon tetrachloride by direct synthesis, according to Le Chatelier's principle, an iron bomb was prepared and filled with a mixture of several brands of active charcoals, including the animal charcoal already used. Liquid chlorine was condensed in the bomb, which was then closed and heated for 60 hours in a sand bath at approximately 170°C. Upon opening, a mixture of solid and liquid chlorides of carbon was found, as well as iron and lead chlorides (the latter from the lead gaskets), but no carbon tetrachloride could be detected.

Thus it is seen that the direct chlorination of carbon by chlorine to form carbon tetrachloride is a reaction that is quite particular as to its catalyst. Stock seems to have struck a charcoal that serves the purpose, though apparently not specially well, but none of the substances we have tested seem to have any value along this line, including a very porous graphite prepared at 4000°C.

It is not impossible, of course, to explain by the catalyst poisoning theory why these two reactions should not reach the calculated equilibrium. It is merely necessary to assume that Bodenstein's catalyst was poisoned by the chlorine which was formed, but not by carbon tetrachloride, whereas Stock's catalyst was affected in exactly the reverse manner. More work along this line will undoubtedly clear up the situation, and show whether some simple assumption is correct, or whether there are complications or an entirely different phenomenon.

THE REACTION $2COCl_2 = CCl_4 + CO_2$

From the thermodynamic data already given, we find for the above reaction $\Delta F^\circ_{298} = -9580$ calories and $\Delta H_{298} = -15{,}870$ calories. Therefore, there is a decreasing tendency for the left-to-right reaction at higher temperatures, assuming ΔC_p to remain small. At about 500°C., however, the carbon tetrachloride equilibrium pressure ought yet to be appreciable and readily determinable, as well as that of carbon dioxide. Stock and Wustrow (25) have calculated several points on the theoretical equilibrium curve, by the use of the heat theorem. We have calculated the position of the equilibrium over a broader band of temperatures, using the thermodynamic data we give above. We have assumed that phosgene has a value of C_p which approximates the average of the values for carbon dioxide and carbon tetrachloride. Therefore ΔC_p will remain small, and will be assumed constant at +3.2, the figure based on our data for 25°C. These data yield:

$$\Delta F^\circ = -16{,}824 - 7.375T \log T + 42\ 5T$$

Starting with this equation, the values for ΔF°, log K, and fractional phosgene pressure have been calculated and are given in table 6.

The formation of phosgene from carbon monoxide and chlorine has been thoroughly studied and commercial-sized plants built for its manufacture (26). Therefore phosgene could undoubtedly be a practical source of carbon tetrachloride, or rather, simply an intermediate product, if a suitable catalyst were found. Quantitative studies of reactions involving phosgene have been made frequently, and for widely varying conditions (27, 28). But seldom have other reactions than $COCl_2 = CO + Cl_2$ and its intermediate steps been investigated, and no carbon tetrachloride has apparently ever appeared when its presence was not desired, or expected. The formation of carbon tetrachloride from phosgene has been reported only by Stock (21, 25), and in very small amounts. The static method he used does not lend itself to accurate results, owing to the small volumes of carbon tetrachloride produced, although it has an important advantage in permitting of long reaction periods. Accordingly, we investigated the decomposition of phosgene by the dynamic method. We decided to attempt to carry out the reaction at as low temperatures as possible, by the use of suitable catalysts if they could be found, to eliminate the multiplicity of other reaction products than carbon dioxide and carbon tetrachloride, such as carbon monoxide, chlorine, hexachloroethane, etc., which complicate the analysis and the interpretation of results.

TABLE 6

Calculated equilibrium for the reaction $2COCl_2 \quad CCl_4 + CO_2$

TEMPERATURE	$1/T$	ΔF°	$-\log_{10}K_p$	PHOSGENE FRACTIONAL PRESSURE
degrees C	*Absolute*	*calories*		
162	0 0023	−6784	−3 41	0 019
203	0 0021	−5984	−2 745	0 041
267	0 00185	−4754	−1 92	0 098
352	0 0016	−3144	−1 10	0 220
496	0 0013	−494	−0 140	0 460

Starting with pure phosgene, the reaction products to be expected at the low temperatures at which carbon tetrachloride will not decompose are carbon dioxide and carbon tetrachloride in equal concentrations and carbon monoxide and chlorine, the formation of which is to be minimized, also in equal concentrations. From the methods mentioned by Olsen (29) for the determination of phosgene, we found the precipitation with aniline most convenient. Chlorine was first removed by means of antimony trisulfide, then phosgene and carbon dioxide by a water solution saturated with aniline and about half saturated with strontium hydroxide. We found that under these conditions phosgene did not hydrolyze and precipitate any strontium carbonate, to interfere with the carbon dioxide determination. Also, the diphenylurea precipitate obtained by the action of phosgene on the aniline was not soluble in the strontium hydroxide solution, though it does dissolve in stronger alkaline solutions. The carbon monoxide and carbon tetrachloride present in the gas mixture were not determined directly. In the apparatus used, phosgene as a gas leaves a cylinder through a needle valve. The rate is measured by a flowmeter containing sulfuric acid, a correction for pressure being applied, for accurate results, from the reading of a special manometer. The phosgene then passes through the reaction tube which contains any catalyst being tested, and is heated electrically. A three-way cock permits the issuing gases to follow a by-pass and be finally exhausted by a water jet suction pump. When the conditions have remained constant a sufficient time, depending on the flow rate and on the age of the catalyst, the cock is turned to permit the gases to enter the absorption train. Liebig bulbs contain the antimony trisulfide and a bubble bottle holds the aniline–strontium hydroxide solution. By regulating line and air admission cocks the pressure in the system can be maintained at slightly above atmospheric. This is to prevent, practically, the entrance of air, which would oxidize phosgene to carbon dioxide, besides introducing a small amount of carbon dioxide otherwise. Perfectly dry antimony trisulfide, the chlorine absorbent, never absorbed any phosgene, nor gave other trouble. The aniline–strontium hydroxide solution was kept and handled entirely like a standard caustic solution, and never touched the air after being prepared. It was kept in a dark bottle to prevent discoloration. In preparing the absorption train flask the train was first filled with pure nitrogen, then the solution admitted. After a run the solution and precipitates were blown back by nitrogen through the gas inlet tube and into a Gooch crucible fitted with an air-tight stopper. After thorough washing with water the crucible was dried to constant weight at 75°C.—24 hours in an electric oven was sufficient—and weighed. The diphenylurea was then leached out by alcohol in a Soxhlet extractor. The crucible was again washed with water and dried at 75°C., the difference in weight being taken as diphenylurea. Now the strontium carbonate was leached out with dilute hydrochloric acid and the crucible washed and dried as before, giving strontium carbonate by difference. The weight of chlorine absorbed was given directly by the gain in weight of the antimony trisulfide tube, as the displaced sulfur remains in the tube. The phosgene used contained some carbon monoxide as impurity. No carbon dioxide and merely the slightest trace of chlorine were found in it, by a blank run. The excess pressure of the cylinder over that of pure phosgene was approximately 5 per cent at the beginning and decreased as more of the gas was used. No hydrogen chloride was found in the phosgene, no test for hydrogen sulfide being obtained after passing over antimony trisulfide.

Experimental

With this apparatus numerous runs were made at 500°C. with the heating tube empty and with different varieties of carbon in it. Animal charcoal gave a substantial decomposition to chlorine and carbon monoxide and gave no carbon dioxide, so it was not used again. Wood charcoals gave little, if any, chlorine, but also practically no carbon dioxide. A very adsorbent and highly activated variety of alkaline black ash charcoal was used in many runs, both alone, and impregnated with solutions of metal salts and then outgassed at a high temperature. Nickel sulfate, copper sulfate, cobalt sulfate, ferric sulfate, and chromium sulfate were used. All of the runs gave the same result, no carbon dioxide, nor, presumably, any carbon tetrachloride. The weights of strontium carbonate obtained averaged about 1.0 mg., and decreased as experimental technique improved. These small weights were probably due to slight infiltration of air. In these runs very little decomposition of the phosgene to carbon monoxide and chlorine occurred, on account of the reaction's sensitivity for a catalyst. Flow rates were as small as 2 cc. per minute, and the heated volume of the tube about 25 cc. The aniline–strontium hydroxide solution was saturated with strontium carbonate, as carbon dioxide-free water was not used in its preparation. All washings were, however, with distilled and recently boiled water, to minimize the solubility of the carbonate.

For its possible interest, a previously used method of analysis will be mentioned, which was perfectly satisfactory for this gas mixture, but is not very sensitive. The issuing gases were passed through gas sampling tubes until at least ten volumes had passed, and then were treated quickly with strong sodium hydroxide solution in a Hempel pipette and gas burette. Simultaneously, a volume of nitrogen was admitted, sufficient to retain the carbon tetrachloride present in the gaseous state. The remaining nitrogen, carbon tetrachloride, and carbon monoxide were passed into another pipette containing some thin paraffin oil saturated with air, and the carbon tetrachloride dissolved quantitatively. The carbon monoxide is lastly determined as usual by means of cuprous chloride. Thus we have determined the volumes of carbon monoxide, of carbon tetrachloride, and of the total gas mixture (that of the sampling tube), sufficient data to calculate the pressure quotient. Phosgene, obtained by difference, constitutes ordinarily the largest part of the total volume, so that little error is introduced in that way. If the gases after the caustic treatment are to be retained over a liquid, mercury should be used, as carbon tetrachloride vapor assumed at 1 atmosphere and 25°C. is soluble in about eight times its volume of water. This method, besides being very rapid, has the advantage that the carbon tetrachloride can be directly recovered afterward.

TABLE 7

Gas absorption by light paraffin oil, at room temperature

RUN NO	CONDITION OF AIR	CONDITION OF OIL	INITIAL VOLUME	FINAL VOLUME	CALCULATED FINAL VOLUME
			cc	*cc*	*cc*
1	Pure, dry	Saturated with air	88 0	88 0	—
2	Pure, dry	Free of air	92 15	92 1	—
3	Saturated with water	Saturated with air	64 6	64 6	—
4	About 50 per cent carbon monoxide	Saturated with air	24 1	24 1	—
5	Saturated with water and carbon tetrachloride	Saturated with air	88 8	76 0	75 95
6	Saturated with water and carbon tetrachloride	That used in No. 5	96 9	82 9	82 88

The oil we used was a standard light paraffin lubricating oil of the following physical properties: density at 27°C., 0.877; flash point, 196°C. (385°F.); fire point, 229°C. (445°F.), both by the Cleveland open cup tester. We found that 15 minutes of gas–oil contact time with frequent shaking was sufficient for equilibrium. In table 7 are given our tests to establish the utility of the method. Run 1 shows that the oil has no appreciable vapor pressure at room temperature; runs 2, 3 and 4 that air, water, and carbon monoxide are practically insoluble in it; and runs 5 and 6 that carbon tetrachloride vapor in small quantities is practically completely dissolved from air. Stock has already shown that concentrated potassium hydroxide solution can effectively dissolve phosgene and carbon dioxide without hydrolyzing carbon tetrachloride appreciably, nor dissolving it.

THE REACTION $CO_2 + CCl_4 = 2COCl_2$

The reverse reaction of the one just discussed, or the formation of phosgene from carbon dioxide and carbon tetrachloride, was next taken up, to attempt to reach the equilibrium experimentally from that side, and to improve on the few and rather unreproducible data of Stock (21).

The apparatus we constructed is shown in figure 6. Carbon dioxide evaporates in the cylinder A and escapes through a needle valve into the system. The flow rate is measured by the oil-filled flowmeter B. The manometer C gives the gage pressure within the saturator D, which contains carbon tetrachloride and is surrounded by a water bath (F) to increase the heat capacity and minimize temperature fluctuations. When lower than room temperatures are desired, running water is employed to cool the saturator. Its temperature is given by the thermometer E. The gases then pass through a bubble bottle containing anhydrous magnesium perchlorate. Next they enter the reaction tube H, which is heated by the electric heater J. A fused nitrate bath is contained in the iron pot I. The issuing gases fill and traverse the gas sampling tubes L and L′, and the issuing phosgene is destroyed by a water jet suction pump.

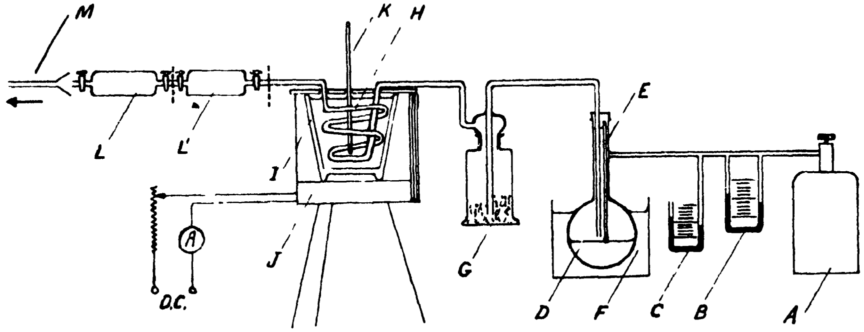

FIG. 6. SET-UP FOR THE FORMATION OF PHOSGENE

The carbon dioxide practically saturated itself with carbon tetrachloride. This can be shown to be true by a brief calculation, knowing a figure for evaporation rate of carbon tetrachloride. The variables will be:

p' = carbon tetrachloride saturation pressure, in atmospheres.

p = actual carbon tetrachloride pressure, in atmospheres.

P = pressure of carbon tetrachloride and carbon dioxide, in atmospheres.

K = rate of evaporation of carbon tetrachloride, in moles per second $\times$ cm^2.

A = Effective liquid area, in cm^2.

Q = moles per second carbon dioxide flow.

$(p'-p)/p' = S$ = fraction of unsaturation.

The result is:

$$\ln S = \frac{-KA(P-p)}{Qp'}$$

Using $K = 6 \times 10^{-6}$, calculated from available data (30), we get $\ln S = -6.2$, or S is 0.2 per cent for our average conditions. As the temperature changes, K and p' should vary somewhat similarly, so that this value of S should hold over the range of room temperatures.

The pressure p' was calculated from the relationship

$$\log p' = 7.8717 - 1732/T$$

which we obtained by plotting data for p' of carbon tetrachloride between 0°C. and 50°C. (4, 30). The best curve through the points plotted as $\log p'$ against $1/T$ is this straight line, and the deviations are quite small. This equation gives the pressure of the liquid in contact with only the pure vapor. Owing to the added carbon dioxide pressure, the change in carbon tetrachloride vapor pressure is given by:

$$(\mathrm{d}p'/\mathrm{d}P)_T = V_l/v_g$$

At 30°C. $\mathrm{d}p'/\mathrm{d}P$ thus amounts to 0.00065, and Dp' is 0.33 per cent of p'. This error is in the opposite direction from that previously calculated for lack of saturation of the carbon dioxide with carbon tetrachloride, and both will be neglected. At the low pressures of 1/6 atmosphere it was assumed that carbon tetrachloride vapor obeys the gas laws closely enough in these calculations.

In the apparatus, the Pyrex helix had a heated volume of 75 cc., and the bath was a eutectic mixture of sodium nitrate and potassium nitrate. This method of heating gives much greater uniformity of temperature than is obtained in a tube in an ordinary electric heater. One side of the pot we thermally insulated better than the other, so that a gentle convection current was obtained. The gases were dried by magnesium perchlorate to prevent carbon tetrachloride hydrolysis and hydrogen chloride formation, which would be included as phosgene in the analytical method finally adopted.

Since the gas mixture after reaction will be entirely composed of carbon tetrachloride, carbon dioxide, and phosgene if there is no chlorine present, only two data are necessary for the analysis, besides this fact. We decided that greatest accuracy would be attained by using: (a) the ratio of moles of phosgene to carbon dioxide in the gases after the reaction, and (b) the ratio of moles of carbon tetrachloride to carbon dioxide before the reaction. (a) can be determined by the usual analytical methods, and (b) from the saturator temperature and pressure. Thus, starting with gas sampling tubes filled with nitrogen it is not necessary to displace the foreign gas completely before the correct result can be obtained. In the chemical analysis standardized solutions of sodium hydroxide, sulfuric acid, and silver nitrate were used. For 50 cc. of the caustic solution the sulfuric acid titre to the phenolphthalein end point was known. After a run, that volume of the caustic was admitted to the sampling tube by a pipette, the tube shaken thoroughly, but not long enough to hydrolyze carbon tetrachloride, and the solution and rinsings were titrated to the same phenolphthalein end point. The decrease in cubic centimeters of sulfuric acid solution required, calculated to moles of the acid, is equal to 1/2 the number of moles of carbon dioxide absorbed plus 3/2 the number of phosgene moles absorbed. The solution was then made to the correct acidity and the moles of phosgene absorbed determined by a Mohr's titration for chloride.

The relationship used in determining the pressure quotient from the data:

$$\frac{p_{CCl_4}}{P - p_{CCl_4}} = \frac{(CCl_4)}{(CO_2)} = R; \quad \frac{(COCl_2')}{(CO_2')} = Q$$

gives

$$K_p = \frac{R}{Q^2} + \frac{R-1}{2Q}$$

of which the latter term may be negligible. The unprimed gas concentrations are for before the reaction; the primed ones are for the gas mixture after reaction.

Experimental

Runs were made with this apparatus at 283°, 314°, 344° and 354°C., both with and without charcoals of different varieties in the tube. The carbon dioxide flow rate was varied between 0.5 and 3.0 cc. per minute. Some runs had to continue for as long as ten hours to yield a sufficient gas sample. In general, the charcoals showed no action, the reaction occurring principally on the Pyrex walls, apparently. We analyzed both gas sampling tubes, each time, and the agreement in the value of Q was generally good, if the conditions had remained uniform, showing that progressive catalyst poisoning was not occurring. New glass and very old glass (Pyrex) both seemed to be active catalytically.

For data by the dynamic method at a lower temperature, a different tube was used—the same one that had been utilized in the attempts to convert phosgene to carbon tetrachloride. It had seen much service, and had crystallized spots, or devitrified, on its inner surface. With otherwise the same apparatus, several runs were made at 250°C.

Many of these runs, in both set-ups, gave low phosgene yields, compared to the rest. These non-equilibrium results were obtained in a quite irregular order, in general, and were not reproducible. In magnitude they extended to perhaps five or ten times the minimum $K(CO_2 \times CCl_4/(COCl_2)^2)$ which was, however, fairly reproducible. The runs in which the maximum phosgene formation was obtained at a given temperature amounted to about one-half the total number, and were relatively fewer at the lower temperatures. It was obvious that the condition of the surface was very important in determining its catalytic effect.

TABLE 8

Experimental results for $CO_2 + CCl_4 = 2COCl_2$

TEMPERATURE	RUN NO	1/K	WEIGHTED AVERAGE 1/K	+log K	1/T	Q	R
degrees C							
354	1	331	316	−2 500	0 001595	0 0293	0 303
354	2	305				0 0316	0 310
344	3	450	435	−2 638	0 001620	0 0243	0 277
344	4	456				0 0244	0 284
344	5	394				0 0259	0 278
344	6	437				0 0236	0 252
344	7	437				0 0232	0 244
344	8	411				0 0135	0 0819
344	9	432				0 0120	0 0683
344	10	451				0 0121	0 0721
314	11	1,212	1,280	−3 080	0 001704	0 0130	0 214
314	12	1,116				0 0137	0 214
314	13	1,365				0 0128	0 229
314	14	1,313				0 0131	0 230
283	15	4,900	4,900	−3 690	0 001799	0 00595	0 175
250	16	16,600	17,100	−4 233	0 001911	0 00388	0 253
250	17	17,600				0 00378	0 255
198	18	458,000	452,000	−5 655	0 002120	0 00073	0 244
198	19	442,000				0 00074	0 242

For temperatures below 250°C. the dynamic method was dropped, as the reaction velocity becomes too slow. Two 2-liter Pyrex flasks were thoroughly dried by heating to almost the softening point for an hour and at the same time passing in a stream of dried carbon dioxide. At least one hundred volumes of carbon dioxide were passed through, insuring the removal of air. Then, weighed quantities of carbon tetrachloride in long thin tubes closed at the bottom were introduced and the flasks sealed off, as quickly as possible. They were placed in a constant temperature oven at 198°C. One was removed at the end of 5 days, and the other at 14 days. The same method for the calculation of K was used as for the dynamic method runs, except that R was calculated from the known volume of carbon dioxide and the weight of carbon tetrachloride. Also, in determining Q it was unnecessary to analyze for carbon dioxide, so distilled water was used to decompose the small amount of phosgene formed and absorb the hydrogen chloride. Thus it was unnecessary to eliminate carbon dioxide before proceeding with the Mohr's titration; instead, neutralization with calcium hydroxide was required. The two bulbs gave almost equal values of K, so that an equilibrium was obtained.

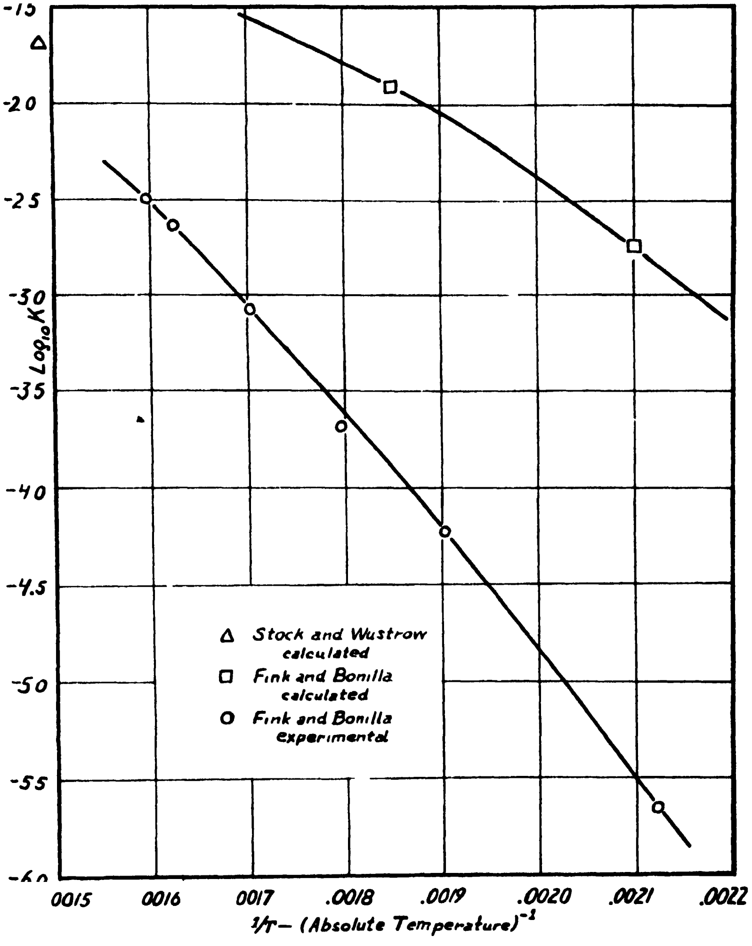

FIG 7 EXTENT OF THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$

The results obtained by all of these methods are given in table 8 In all of these phosgene formation runs no chlorine was ever noticed, by smell or by the iodide–starch test, owing undoubtedly to the fact that no catalyst for its formation was present. So the reaction was not complicated by the decomposition of carbon tetrachloride or that of phosgene to carbon monoxide and chlorine. Undoubtedly phosgene was formed in every case, as it could be detected by its distinctive smell even in the lowest concentrations. No hydrogen chloride was ever noticed after a run was well started.

The results have been plotted in figure 7, and approach the theoretical curve as the temperature rises. It is noticed that the point at 283°C. does not quite fall on the curve with the rest. This was the lowest temperature at which the first heating coil was used, and probably the corresponding equilibrium was not reached, owing to diminished speed of reaction, that was reached at the higher temperatures. It was practically impossible to operate at flow rates small enough to reach equilibrium at below 300°C. for this first coil, or at below 250°C. for the old tube. Five-tenths of 1 cc. of carbon dioxide per minute was the lowest rate found feasible.

The fact that a different tube, in the case of the point at 250°C. and an entirely new method at 198°C., gave points on a smooth curve that is almost straight seems to bolster up the possibility that a real metastable or false equilibrium is reached in this reaction, which similarly may be true for other reactions; $C + 2Cl_2 = CCl_4$ has already been considered, and $2COCl_2 = (COCl_2)_2$ has been mentioned.

The constant volume small bomb results of Stock (21) are naturally not of the same degree of accuracy as these based on the dynamic method. Stock could only produce a few hundredths of a cubic centimeter of phosgene in a bomb. For the production of carbon tetrachloride by the reverse of the reaction now being considered he has fairly good checks in two runs (31) at 400°C. and two at 500°C. The values of $(COCl_2)^2/(CO_2) \times (CCl_4)$ we obtain from his data are $\log^{-1} 2.77$ at 500°C. and $\log^{-1} 3.77$ at 400°C. These points bear out the false equilibrium theory, but were not plotted in figure 7 because the curves now shown would be dwarfed.

We believe that we have really reached an equilibrium. It may be the end of a fast reaction, with another slow one occurring simultaneously, which will eventually lead the system to the theoretical equilibrium. It is not possible at present to tell whether such a slower reaction exists, but from our data and those of Bodenstein and of Stock it is apparent that such a slower reaction must indeed be slow, compared to the observed one. This statement also holds for the other previously mentioned "false equilibria." In table 9 are given data for runs at 344°C. at higher flow rates than the minimum ones used. The pressure quotient obtained is plotted in figure 8 against the carbon dioxide flowmeter reading, which is practically proportional to the carbon dioxide mass flow at the low flow rates used. It is seen that extrapolation to zero flow rate along the simple curve gives practically the same value for the extent of reaction as that obtained at the lowest flow rate that was actually used. In carrying out the extrapolation it should be remembered that at zero flow rate the curve should approach the pressure quotient axis normally. For simplicity we did not

TABLE 9

Effect of flow rate variations on the extent of reaction of $CO_2 + CCl_4$ $2COCl_2$ *at 344°C.*

RUN NO.	FLOWMETER	1/*K*	WEIGHTED AVERAGE 1/*K*	log *K*	*Q*	*R*
	mm.					
3 to 10	3.4		435	−2.638	0.024	0.26
20	22 0	3,080	2,960	−3.472	0.00885	0.244
21	22 0	2,840			0 00920	0.244
22	16.5	1,090	1,200	−3 080	0.01446	0.234
23	16.5	1,490			0.01259	0.241

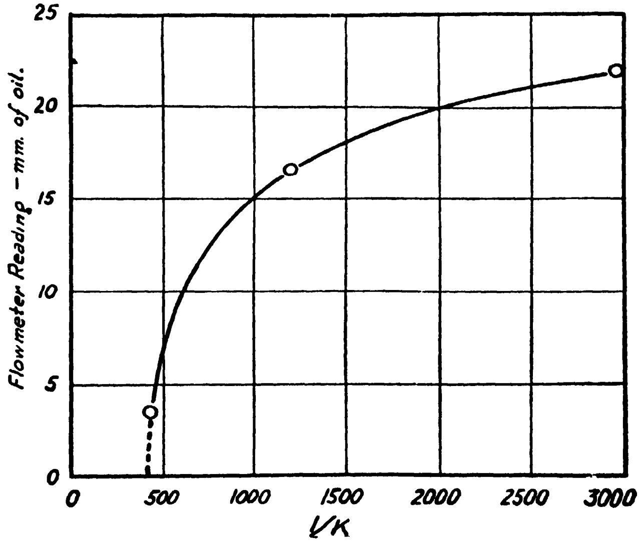

FIG. 8. EFFECT OF FLOW RATE ON THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$ AT 344°C.

apply this slight correction for finite reaction time, owing to its small magnitude under the conditions and to the additional amount of data that would have been required at the various temperatures. We do not feel that these data are sufficiently accurate to merit calculation of the velocity constant, etc.

A careful consideration of the experimental facts seems to point more strongly to the existence of a false equilibrium of unknown mechanism than to a simple catalyst poisoning, as advocated by Bancroft (31), for false equilibria in bomb reactions. Bancroft does not mention the dynamic method. The principle argument for catalytic surface poisoning in this reaction is given by the consideration that over a rather broad range of gas phase compositions, between the two false equilibrium curves, the forward and reverse reaction velocities are equal, or almost equal if a slight drift towards the true equilibrium exists. It is hard to conceive of this being so unless the two velocities are each zero, or almost so, and the simplest explanation for this would be a poisoned catalyst, unable to allow either forward or reverse reaction to proceed.

In support of some other mechanism as causing the false equilibria let us consider the possible explanations according to the poisoned catalyst theory. False equilibrium might be expected, owing to one of the following phenomena: (1) any one or more of the reactants being strongly and reversibly adsorbed by the catalytic surface (excluding others); (2) any reactant or outside substance being strongly and irreversibly adsorbed, forming a compound of very low dissociation pressure, deactivating the surface. According to the first possibility the reaction velocity would decrease rapidly but smoothly as the pressure of the strongly adsorbed substance increased. However, the composition of the gas phase in equilibrium with the catalyst could not vary, according to the principles of thermodynamics, or, to be more accurate, the equilibrium pressure-constant calculated for the gas phase cannot depend on the nature of the catalyst surface. Our value of the pressure quotient therefore does not depend on the reversible absorption of one of the reactants, assuming equilibrium to have been practically reached. Furthermore, if the reaction velocity in one direction were decreased by stronger adsorption of the product, that in the opposite direction with the same catalyst would be increased, and none of the reactions have been found to take place as readily as this would indicate. For instance, the same tube that was utilized for the reaction $CO_2 + CCl_4 = 2COCl_2$ at 250°C. gave no indication whatsoever of the reverse reaction, as has already been mentioned. The second above possible explanation obviously cannot be true in this case, in which the extent of reaction was never found to vary consistently with the age of the catalyst, or length of the run.

To supply somewhat of a check on the results, runs 8 to 10 were performed, in which the relative amounts of the gases in the issuing equilibrium mixture were varied by cooling the carbon tetrachloride evaporator. Compared to runs 3 to 7, at the same temperature and flow rate, the equilibrium phosgene concentration has decreased to about one-half and the carbon tetrachloride concentration to about one-fourth of the values for the previous runs. The pressure quotient K is seen to remain the same, in fact the average K's for the two groups of runs are so similar that the agreement is partly fortuitous, as can be told from the magnitude of the individual deviations.

A third possible explanation of the results obtained is that one of the products, say phosgene, might reversibly combine with the solid catalyst to form a solid compound, of appreciable dissociation pressure, that has no catalytic properties. There would, from the phase rule, be only one equilibrium pressure of phosgene at any temperature, if both solid phases were present. Therefore it would not be possible to produce the poison phosgene, say, at a pressure higher than this pressure for equilibrium with the poisoned catalyst, and one would be measuring the dissociation pressure of this poisoned catalyst rather than the gas reaction equilibrium. This state of affairs would also give the same false equilibrium with the streaming method as with bomb reactions. However, this is probably not the explanation in this case, as many factors oppose it. In the first place, the same catalyst could not cause each of two opposing reactions to take place, separately, even to a slight extent, as Stock has succeeded in doing for the forward and reverse reactions of $CO_2 + CCl_4 = 2COCl_2$. In the second place, the calculated K would vary as the initial ratio R were varied, whereas runs 8 to 10 show no variation. Finally, if such a poisoned catalyst compound is formed, a little reasoning will show that a smooth curve of flow rate (or time of reaction) against K or fraction decomposed would not be obtained; there would be a discontinuity at the flow rate at which the time of reaction were just sufficient for the reaction to have proceeded to the point where the phosgene pressure produced equaled the poisoning phosgene pressure. Figure 8 seems to indicate that this is not so, although obviously there are not enough points to make the argument strong.

SUMMARY

We have investigated several little-known reactions by which carbon tetrachloride might be commercially produced. With this purpose in mind we have coordinated the previous work in this field and carried out similar and other experiments of our own.

We have concluded that a number of these reactions, generally chlorinations of carbon compounds or of carbon itself, and other related reactions, differ inherently in the manner in which they occur, from those between carbon and oxygen, sulfur, or even hydrogen. A great deal of further work is necessary to clear up the subject.

A detailed summary follows:

Theoretical calculations

1. A series of new thermodynamic data has been calculated from available data. The results include C_p of carbon tetrachloride vapor at 1 at-

mosphere from 0°C. to 300°C., S_{298} of silicon dioxide (quartz), $C_{p,298}$ of phosgene at 1 atmosphere, and ΔF°_{298} of formation of silicon tetrachloride (g), stannic chloride (g), aluminum chloride (g), and silicon dioxide (quartz).

2. The equilibrium constant for the reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$ was calculated from experimental data of Weiser and Wightman.

3. A convenient and accurate method was developed for obtaining the equilibrium constant of the reaction, $CO_2 + CCl_4 = 2COCl_2$, involving saturating carbon dioxide with carbon tetrachloride at a known temperature and analyzing the equilibrium mixture for $(COCl_2)/(CO_2)$ ratio.

Experimental work

4. It was shown theoretically and supported experimentally that it is not possible to carry out appreciably the reaction $COCl_2 + 2MeCl = CCl_4 + Me_2O$, where Me is an equivalent of a metal. Ultra-violet light was shown to displace the equilibrium, in one case, towards the right.

5. Ordinary animal charcoal was found to be a good catalyst for the reaction $CCl_4 = C + 2Cl_2$, but experimental confirmation could not be obtained of the reverse reaction.

6. The reaction $2COCl_2 = CO_2 + CCl_4$ was attempted in both directions and the reverse reaction quantitatively studied, and indications were obtained of the existence of an undetermined factor which prevents the reaching of the theoretical equilibrium.

7. A new method for the volumetric analysis of carbon tetrachloride mixed with other gases was developed, tested and found satisfactory. Also, a method for the continuous absorption of chlorine, phosgene and carbon dioxide and determination of their proportions was devised and found satisfactory.

REFERENCES

(1) Eyring, H.: J. Am. Chem. Soc. **54**, 3191 (1932).

(2) Duhem, P.: Traité de Mecanique Chimique, Vol. I, p. 227. A. Hermann, Paris (1896).

(3) Hood, H., and Murdock, H.: J. Phys. Chem. **23**, 498 (1919).

(4) International Critical Tables. McGraw-Hill Book Co., New York (1927).

(5) Partington, J. R., and Schilling, W. G.: Specific Heats of Gases. Ernest Benn, London (1924)

(6) Partington, J. R.: Chemical Thermodynamics, p. 42. D. Van Nostrand, New York (1924).

(7) Sutherland, W.: Phil. Mag. [5] **26**, 298 (1888).

(8) Parks, G. S., and Huffman, H. M.: The Free Energies of Some Organic Compounds, p. 196. The Chemical Catalog Co., New York (1932).

(9) Chipman, J.: Ind. Eng. Chem. **24**, 1014 (1932).

(10) Maier, C. G.: Bur. Mines Tech. Paper No. 360 (1925).

(11) Roth, W. A.: Z. physik. Chem. **144**, 253 (1929).

(12) Maier, C. G.: J. Am. Chem. Soc. **51**, 194 (1929).

(13) Weiser, H., and Wightman, G.: J. Phys. Chem. **23**, 415 (1919).

(14) Kharasch, M. S.: Bur. Standards J. Research **2**, 418 (1929).

(15) Leermakers, J., and Dickinson, R.: J. Am. Chem. Soc. **54**, 4648 (1932).

(16) Berthelot: Ann. chim. phys. [6] **28**, 126 (1893).

(17) Regnault, V.: Ann. chim. phys. [2] **71**, 385 (1839).

(18) Bolton, W.: Z. Elektrochem. **9**, 209 (1903).

(19) Demarcay, E.: Compt. rend. **104**, 111 (1887).

(20) Camboulives, P.: Compt. rend. **150**, 175 (1910).

(21) Stock, A., et al.: Z. anorg. Chem. **195**, 140 (1931).

(22) Dodge, B.: Ind. Eng. Chem. **24**, 1353 (1932).

(23) Bodenstein, M., and Gunther, P.: Z. angew. Chem. **43**, 423 (1930).

(24) Stock, A., et al.: Z. anorg. Chem. **195**, 149 (1931).

(25) Stock, A., and Wustrow, W.: Z. anorg. Chem. **147**, 245 (1925).

(26) Atkinson, R. H., et al.: J. Chem. Soc. **117**^{2}, 1410 (1920).

(27) Almasy, F.: Naturwissenschaften **19**, 270 (1931).

(28) Bodenstein, M., Lenher, S., and Wagner, C.: Z. physik. Chem. **3B**, 459 (1929).

(29) Olsen, J. C., et al.: Ind. Eng. Chem., Anal. Ed. **3**, 189 (1931).

(30) Carbon Tetrachloride, a booklet issued by the Roessler and Hasslacher Co., New York.

(31) Bancroft, W. D.: J. Phys. Chem. **22**, 22 (1918).

ON THE MECHANISM OF GASEOUS REACTIONS. I

The Thermal Decomposition of Methyl Ethyl Ether

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In recent years a great deal of attention has been focussed on the study of the kinetics of homogeneous gaseous reactions, in particular those of thermal decomposition processes. In a considerable number of cases it has been found that the rate follows a first order equation which corresponds to a unimolecular mechanism. As a general rule the more complex molecules tend to decompose at a unimolecular rate, and the field of organic chemistry has proved particularly fruitful in providing examples. Accurate measurements of rates have led to the development of a number of theories regarding the mechanism of the activational process, the most successful of which have made use of energy supplied at molecular collisions, taking into account the internal degrees of freedom of the molecules (1). The decrease in rate when the pressure is lowered, which is characteristic of a number of unimolecular reactions, is a necessary consequence of such theories. The radiation hypothesis (2), which ascribed activation to the absorption of infra-red radiation by the molecules of the reactant, in its general form unfortunately permits of no comprehensive experimental test, largely on account of the difficulties connected with manipulation in the infra-red (3).

In many of the reactions studied the problem of working out the kinetics of the process is complicated by the fact that there may be several ways in which the molecule can break up, and the decomposition is not a single reaction but involves concurrent and consecutive processes. It is often possible, however, either to neglect or to correct approximately for these complications, since one reaction may predominate as the rate-determining step. This is fairly satisfactory where side reactions involve only a small fraction of the reacting substance, and where subsequent processes are either too slow or too fast to interfere with the primary rate, but this of course cannot always be the case. Where reactions are studied over wide ranges of temperature and pressure, the relative effects of the various processes involved may vary considerably, and this may invalidate conclusions of a theoretical nature which are based on the assumption of a single reaction mechanism.

It is therefore of considerable importance that deviations from simple uni- or bi-molecularity be investigated with regard to the possibility of complicating reactions, and the kinetics of the various processes be worked out where possible. One such case has been studied by Clusius and Hinshelwood (4), in the catalytic decomposition of diethyl ether.

The present article deals with a study of the decomposition of methyl ethyl ether, in which case marked deviations from a simple unimolecular course have been observed. This decomposition has been studied by Glass and Hinshelwood (5), who noted approximate unimolecularity but state that "the reaction is far from being an ideal example of a unimolecular change." The results here reported disagree in some respects with those of these two authors, our rates being uniformly lower. We have noted, however, a marked catalytic effect produced by the presence of small quantities of alkyl iodide such as may be introduced into the ether during its preparation. The second article of this series will deal with this phase of the work.

EXPERIMENTAL

The course of the decomposition process was followed by observing the pressure increase when samples of the gas were maintained at constant temperatures and volume in a Pyrex glass reaction tube.

Apparatus

The experimental arrangements are shown diagrammatically in figure 1. Vessels A, B, and C constitute a train for the preparation and purification of the ether, and D is a storage flask of 1-liter capacity provided with the manometer M_2. Several reaction chambers, E, were used, these being of Pyrex with about 125-cc. capacity. Connection with the storage flask was provided at stopcock T_1, and with diffusion or Töpler pumps at T_2, all connecting tubing being of capillary size. Pressures were measured on the constant-volume manometer H operated by the levelling device G. The gas space outside the furnace was small compared with the total. An electric furnace was used for heating, and the fluctuations in line voltage during a run were compensated by the use of a slide wire resistance operated by hand. Since the furnace and reaction tube were heated for two to three hours prior to each run, the above method of regulation was found to be quite satisfactory. Temperatures were measured by the platinum resistance thermometer I, in some cases a thermocouple being inserted as a check. For the early runs the temperature variation was of the order of 2°C., while for later runs on which most of the conclusions are based the temperature was controlled to within 0.8°C. The absolute values of the temperature are probably correct to 2°C.

Since there is always some uncertainty in obtaining the initial pressure of gas by direct measurement, it was found to be more satisfactory to continue each experiment until a constant final pressure was recorded and to use this value to obtain the initial pressure. The ratio of initial to final pressures was determined accurately at several temperatures by admitting gas to the cold reaction chamber, followed by heating until decomposition was complete. It turned out that this ratio was constant over the temperature range employed.

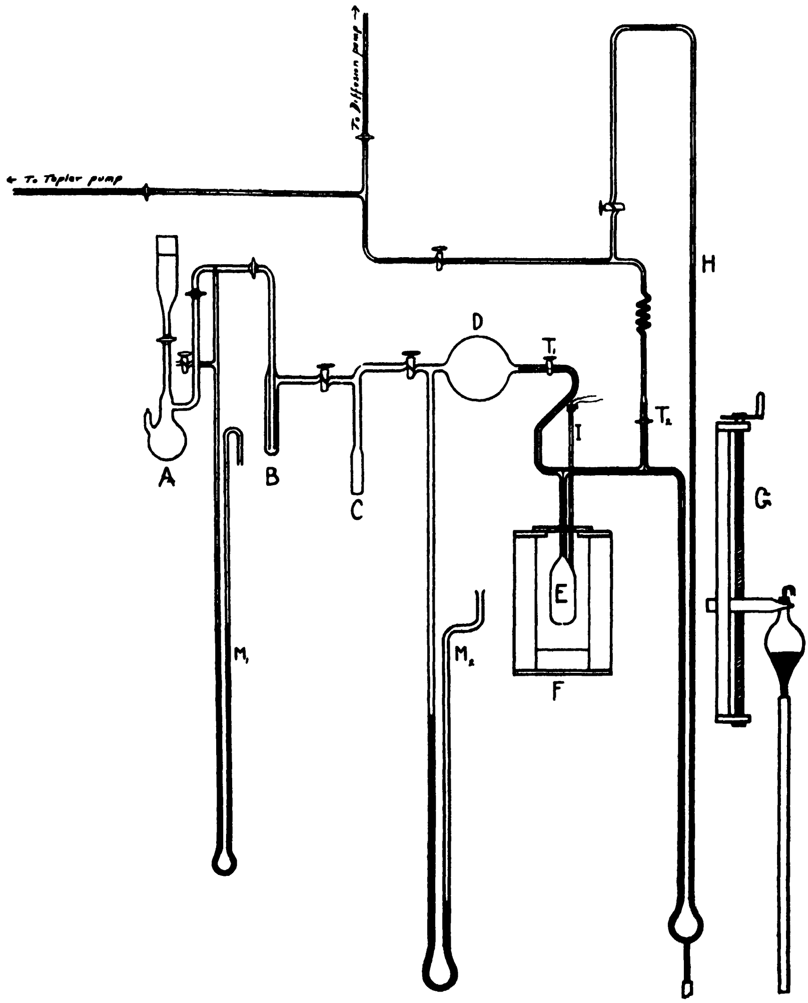

FIG. 1

Preparation of the ether

Methyl ethyl ether was prepared according to the historic method of Williamson (6), by allowing sodium methoxide to react with ethyl iodide, followed by distillation. Several samples were prepared, and modifications of procedure and apparatus were introduced to improve yield and purity of product. A number of rate measurements were made on samples prepared under various conditions, and it was observed that rates varied considerably from sample to sample. The discrepancy was traced to the presence in the final product of small quantities of ethyl iodide, which were found to exert a marked catalytic effect on the decomposition rate. The procedure finally adopted to ensure the elimination of ethyl iodide was as follows (sample 5): Eight grams of sodium were allowed to react completely with 75 cc. of absolute methyl alcohol. The resulting solution of sodium methoxide in the excess alcohol was run into the flask A, which had previously been evacuated. A quantity of ethyl iodide (23 cc.) less than the calculated amount was then admitted and the mixture allowed to stand for 6 days. It was then heated to 45°C. and a fraction of about 7 cc. distilled over into tube B, which was immersed in liquid air. Here the distillate came in contact with metallic sodium which served to remove methyl alcohol. Tube B was warmed to room temperature and some gas released through the stopcock at the manometer. The ether was then condensed in tube C at $-10°$C., cooled with liquid air, and permanent gases pumped off. The product was distilled back into tube B for further treatment with sodium, returned to C, cooled in liquid air once more, and the system evacuated. The ether was then allowed to expand into the reservoir. With the above quantities a pressure of 60 cm. at room temperature was obtained.

Analysis of the products of reaction

The gas mixture from the reaction chamber was pumped off with the Töpler pump, collected in a gas burette over water (or over mercury in the cases of partial decomposition), and the constituents determined in the usual manner. Undecomposed ether was determined by absorption in cold concentrated sulfuric acid, hydrogen by palladinized asbestos or copper oxide; in the latter case the gas mixture was passed slowly back and forth over the oxide at 280°C. ten or twelve times. Methane and ethane were determined by explosion.

To detect the presence of aldehydes in the gases from incomplete decomposition the silver mirror test was applied to a few cubic centimeters of water which had been standing in contact with the gas. To distinguish between formaldehyde and acetaldehyde the gas mixtures were allowed to stand in contact with about 10 cc. of ethyl alcohol in the Töpler pump. A portion of this solution was then tested for acetaldehyde by heating with sodium hydroxide. Even small concentrations of acetaldehyde produce a yellow color and distinctive odor (7). For formaldehyde, heating a portion of solution with 0.05 g. of resorcinol and 50 per cent sodium hydroxide produced a pink shade (8). Estimation of quantities in both tests was made by color comparison with known solutions.

RESULTS

The products of the reaction

The complex nature of the decomposition process may be seen from the diversity of the products as given in table 1 Here are shown the percentages of the various constituents found in the gas mixture after the reactions had been carried to completion. The discrepancies in the totals may be due to the small volumes analyzed in some cases. The presence of considerable hydrogen in all cases is interesting, since Glass and Hinshelwood report no hydrogen. The gas mixture shows approximately the same composition at the different temperatures of decomposition, and is much the same for the different samples of ether prepared, although as mentioned above there is reason to believe that the decomposition process was somewhat different in the cases of samples 2, 3, and 4, than for sample 5.

TABLE 1

Products of the thermal decomposition of methyl ethyl ether

TEMPERATURE	ETHER SAMPLE	CARBON DIOXIDE	UNSATURATEDS (C_2H_4)	OXYGEN	CARBON MONOXIDE	HYDROGEN	METHANE	ETHANE	TOTAL
degrees C		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
509	2	2 2	4 0	0	28 3	5 7	53 8	2 0	96 0
510*	3	0	0	1 0	33 3	1 1	55 7	4 7	95 8
456	4	0	4 0	0 8	30 8	4 0	55 6	4 7	99 9
457	5	0	5 1	0 8	33 1	8 4	45 2	6 5	99 1
487	5	2 9	0 7	0 7	31 8	9 8	52 7	4 4	103 0
509	5	0 2	1 8	0 5	32 0	9 4	50 5	5 6	100 0

* Reaction bulb packed with glass rods.

In a series of experiments the gas was removed from the reaction chamber before the reaction was complete, in order to obtain evidence of the presence of aldehydes as intermediate products, and to compare the other products with those obtained at the end of the reaction.

While both formaldehyde and acetaldehyde were detected the concentration of the former was always very small, while that of the acetaldehyde was appreciable. Thus when the pressure had increased by 50 per cent at 490°C., the pressure of formaldehyde in the reaction chamber was estimated at 0.08 cm., and that of acetaldehyde at 14.5 cm. At 565°C. at a pressure 2.3 times the initial there was found a trace of formaldehyde and about 5 cm. of acetaldehyde. The proportions of the other constituents in some of these experiments are shown in table 2.

As a result of these analyses the steps in the decomposition process would appear to be the following:

$$CH_3OC_2H_5 \rightarrow CH_3COH + CH_4 \qquad (1)$$

$$CH_3OC_2H_5 \rightarrow HCOH + C_2H_6 \qquad (2)$$

$$CH_3COH \rightarrow CH_4 + CO \qquad (3)$$

$$HCOH \rightarrow H_2 + CO \qquad (4)$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad (5)$$

Reaction 1 followed by reaction 3 seems to be the predominating process, the analyses indicating that about 65 per cent of the ether decomposes according to reaction 1 at all temperatures. The decomposition of the formaldehyde according to equation 4 appears to be fast compared with that of the ether, while that of acetaldehyde may be relatively slow, as shown by the concentrations of this compound obtained during the course of the reaction. The equilibrium between ethane and its products (equation 5) accounts for the presence of ethylene, and it is to be expected that this equilibrium would be established in the temperature range used (9).

TABLE 2

Products of the partial decomposition of methyl ethyl ether (sample 5)

TEMPERATURE	ETHER SAMPLE	ETHER	CARBON DIOXIDE	UNSATURATEDS (C_2H_4)	OXYGEN	CARBON MONOXIDE	HYDROGEN	METHANE	ETHANE	TOTAL
degrees C		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
400	5	24 3	0	6 8	1 0	32 2	5 1	37 9	11 6	94 6
486	5	11 9	0	1 7	0 6	31 2	7 5	52 5	7 9	101 4
507	5	26 4	0	4 5	1 2	38 7	8 3	41 2	3 2	96 4

The above processes produce somewhat over three moles for one, so that the pressure at the end of the reaction should be over three times the initial pressure. It was found, however, that the final pressure was only 2.70 times the initial at a series of temperatures within the range of the experiments. This means that some non-gaseous products are formed, the nature of which has not been determined. Whether these are formed from the original ether or from the intermediate products is not evident from the results, bút since the extent of this condensation seems to be independent of temperature it will not greatly affect the conclusions here obtained.

The kinetics of the decomposition

That the reaction as a whole is approximately a first order process in most cases is illustrated in table 3, which shows a summary of the majority of the complete runs which were carried out. The columns headed t_{25}, t_{50}, and t_{75} show the time in minutes for the pressure increase to reach 25 per cent, 50 per cent, and 75 per cent, respectively, of its final value. The last three columns show the ratios $t_{25}:t_{50}:t_{75}$, with t_{50} taken as unity. For a unimolecular process these ratios should be 0.415:1:2, while for a bimolecular they should be 0.333:1:3. The numbers corresponding to the sample of ether from which the gas sample was drawn are shown in the second column. The time values vary remarkably from sample to sample at corresponding temperatures and those for sample 5 are the largest, indicating the slowest rates. This variation as mentioned above has been shown to be attributable to the presence in samples 2, 3, and 4 of traces of ethyl iodide acting as a catalyst.

TABLE 3

Summary of the majority of the complete runs

NO	ETHER SAMPLE	TEMPERATURE	INITIAL PRESSURE	t_{25}	t_{50}	t_{75}	t_{25} t_{50} t_{75}
		degrees C	*cm*	*minutes*	*minutes*	*minutes*	
4	2	503	11 92	7 4	15 0	32 5	0 493:1:2 16
5	2	509	7 7	7 5	18 9	40 4	0 397:1:2 14
8	3	510	17 3	1 0	2 1	4 0	0 476:1:1 91
9*	3	510	15 1	2 5	30 6	110 2	0 082:1:3.60
10†	3	510	14 7	4 7	12 5	40 0	0 376:1:3 20
12†	3	487	14 4	5 0	13 5	31 8	0 370:1:2 36
14	3	487	13 4	2 4	5 3	10 4	0 453:1:1 93
15	3	487	3 2	7 4	15 9	30 0	0 465·1·1 89
16	4	456	10 25	8 9	29 5	64 7	0 302:1:2 19
30	5	457	29 66	151 4	377 6		0 401.1: - -
25	5	487	24 96	28 6	66 7	146 3	0 429:1:2 20
29	5	488	30 44	25 8	66 4	169 2	0 389:1:2 55
26	5	509	29 9	13 8	34 3	91 0	0 402:1:2 65
37	5	510	23 6	12 3	33 0	89 5	0 373:1.2 71
32	5	565	28 7	0 77	2 32	8 0	0 331.1·3 45

* Bulb packed with glass wool.

† Bulb packed with glass rods.

Runs 9, 10, and 12 were made with the reaction chamber packed with glass wool or glass rods and show a marked decrease in rate, which is connected with the catalytic behavior.

In interpreting the mechanism of the decomposition process, only those experiments made with ether sample 5 will be considered here, for the reasons advanced above. The treatment of the catalyzed reaction will be taken up later.

It was first noticed that at the lowest temperature used the process is very closely a unimolecular one. This is shown in table 4 for an experiment at 457°C. The pressures given in the second column were taken from a smoothed curve of the experimental data which was extrapolated back to the initial pressure for zero time, and the values of the unimolecular constant k_1 are calculated over 20-minute intervals. This may be interpreted as meaning that the rate-determining step at 457°C. is the primary decomposition of the ether, and the subsequent reactions are rapid. That is, the decomposition even of the acetaldehyde is fast compared with that of the ether.

TABLE 4

Decomposition of the ether at 457°C.

Initial pressure, 29.66 cm.

t	P	$k_1 \times 10^3$
minutes	*cm*	*min* $^{-1}$
0	29.66	
20	31.30	1.65
40	33.05	1.82
60	34.75	1.84
80	36.45	1.91
100	38.15	1.99
120	39.85	2.07
140	41.45	2.01
160	42.90	1.92
180	44.30	1.91
200	45.60	1.85
220	46.80	1.77
240	48.00	1.83
260	49.15	1.82
280	50.30	1.90
300	51.40	1.88
320	52.40	1.77
340	53.35	1.75
360	54.20	1.61
380	54.95	1.46
400	55.65	1.42
		Av. = 1.81

As the temperature is raised, however, this is no longer the case, and the higher the temperature the greater the deviation from the simple mechanism. This is shown in figure 2 in which log $(P_f - P)$ is plotted against the time for a number of runs, where P_f is the final pressure and P the pressure as measured throughout the course of the reaction. For a unimolecular reaction of course this plot should give a straight line, and this is practically the case at 457°C. At 487°C. the deviation is not very great, the calculated constant first increasing and then decreasing during the course of the reaction. The values at this temperature are given in table 5.

The greatest deviation is shown in the experiments at 565°C., and here calculation shows that the rate-determining step is practically bimolecular. This is shown in table 6 where the bimolecular constant is obtained from the values of $\frac{1}{P_f - P}$ throughout the reaction. In this case a correction has been applied to the value of P_f to take into consideration the subsequent decomposition of ethane, which is apparently much slower than the main process.

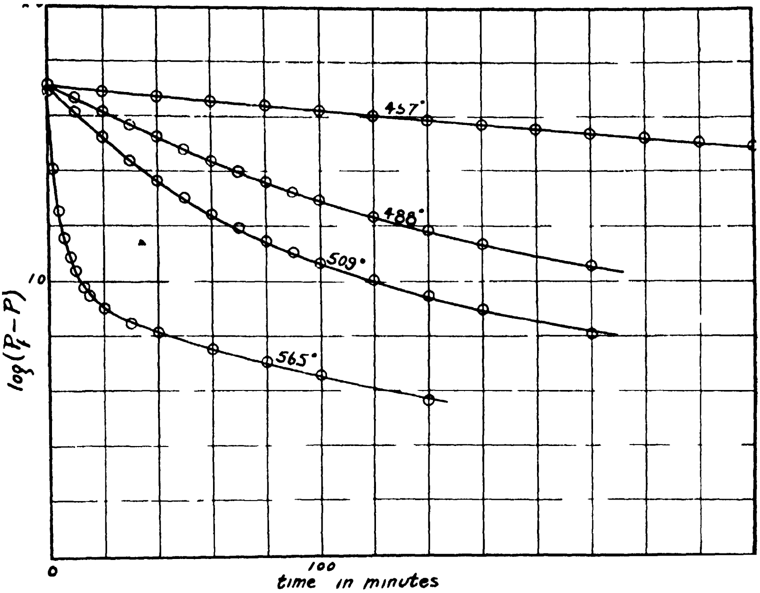

FIG. 2

The bimolecular decomposition of acetaldehyde has been studied by Hinshelwood and Hutchison (10) and the value of the constant at 565°C. taken from the work of these authors is shown in the table. k_2 as obtained here is considerably smaller, but of the same order of magnitude.

The explanation of this bimolecular rate is then that the decomposition of acetaldehyde is the rate-determining step, the primary decomposition of the ether taking place very rapidly by comparison, so that in the early stages of the process the ether is practically completely decomposed.

TABLE 5

Decomposition of the ether at 487°C.

Initial pressure, 24 96 cm.

t	P	$k_1 \times 10^2$
minutes	*cm*	*min* $^{-1}$
0	24 96	
10	28 85	0 96
20	32 60	1 02
30	36 10	1 06
40	39 25	1 06
50	42 17	1 09
60	44 73	1 07
70	46 85	0 95
80	48 68	0 96
90	50 25	0 87
100	51 63	0 83
120	53 87	0 76
140	55 68	0 72
160	57 30	0 74
200	59 60	0 64

TABLE 6

Decomposition of the ether at 565°C.

Initial pressure, 28.7 cm

t	P	$P_f - P$	$k_2 \times 10^2$
minutes	*cm*		*cm* $^{-1}$ *min* $^{-1}$
0	28 7	44 95	
1	40 8	32 85	0 82
2	52 1	21 55	1 59
3	56 7	16 95	1 26
4	59 85	13 80	1 34
5	61 95	11 70	1 31
6	63 4	10 25	1 20
7	64 5	9 15	1 19
8	65 4	8 25	1 19
9	66 15	7 50	1 21
10	66 8	6 85	1 26
15	68 8	4 85	1 20 Av. = 1 23
20	69 7	3 95	0 94
30	70 6	3 05	0 75

Final pressure of ethylene taken as 4 cm. k_2 for acetaldehyde at 565°C. (Hinshelwood and Hutchison) =,2.09 × 10^{-2} cm.$^{-1}$ min.$^{-1}$

At intermediate temperatures both processes should be proceeding at measurable rates, and the process then consists in the main of a unimolecular reaction followed by a bimolecular one. Such a mechanism does not permit of simple mathematical treatment, but an attempt has been made to obtain a certain correlation of the results.

The total pressure P at any time t during the reaction will on the assumptions outlined above be given by

$$P = P_f - (P_f - P_i)\, e^{-k_1 t} - b \tag{1}$$

where P_f is the final pressure, P_i the initial pressure, k_1 the unimolecular constant for the total ether decomposition, and b the pressure due to the acetaldehyde present. Here the formation of condensed products if from the original ether is assumed to be a first order process; if from intermediate products then the rate must be fast. The formation of ethylene from ethane is not taken into consideration, but if this takes place only at a later stage in the process, then the value of P_f in the above equation will have to be modified accordingly.

Now the pressure due to acetaldehyde is changing at the rate given by

$$\frac{\mathrm{d}b}{\mathrm{d}t} = 0\ 65\, k_1\, P_i e^{-k_1 t} - k_2 b^2 \tag{2}$$

where 0.65 k_1 represents the part of the rate constant which refers to the decomposition of the ether to acetaldehyde, and k_2 is the bimolecular constant for acetaldehyde.

Equation 2 unfortunately has no finite solution, so that it is necessary to make use of it in the differential form.

Differentiating equation 1 we obtain

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_1\,(P_f - P_i)\, e^{-k_1 t} - \frac{\mathrm{d}b}{\mathrm{d}t}$$

and combining with equation 2,

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_1\,(P_f - 1.65\, P_i)\, e^{-k_1 t} + k_2 b^2 \tag{3}$$

Now the value of k_1 may be estimated from the following considerations. Near the beginning of the process b is very small and hence $k_2 b^2$ in equation 3 may be neglected. This equation integrated then gives

$$P = (P_f - 0\ 65\, P_i) - (P_f - 1.65\, P_i)\, e^{-k_1 t}$$

or

$$\log\,(P_f - 0.65\, P_i - P) = \log\,(P_f - 1.65\, P_i) - \frac{k_1}{2\ 303}\, t \tag{4}$$

k_1 may then be obtained from a series of the values of P near the beginning of the reaction for which equation 4 is linear.

Having k_1, values of b throughout the reaction are obtained from equation 1, and then values of k_2 from equation 3, making use of slopes of tangents to the experimental pressure–time curve to obtain $\frac{dP}{dt}$.

The results of applying this method of treatment to an experiment at 509°C. are shown in table 7.

The value of k_1 using equation 4 comes out to be 0.0387. The second column shows the experimental values of total pressure throughout the experiment. Values of b and k_2 are obtained using equations 1 and 3. The column headed P_e gives the pressure due to undecomposed ether at the corresponding times, the values being obtained from the first order equation

$$P_e = P_i e^{-k_1 t}$$

TABLE 7

Decomposition of the ether at 509°C

Initial pressure, 29 9 cm ; k_1 = 0 0387 min $^{-1}$

	P	P_e	b	$k_2 \times 10^3$
minutes	*cm*	*cm*	*cm*	*cm* $^{-1}$ *min* $^{-1}$
0	29 90	29 90	0	
10	39 50	20 30	5 70	4 4
20	47 40	13 80	8 20	2 47
30	53 25	9 38	9 45	1 64
40	57 50	6 38	10 00	1 16
50	60 65	4 31	10 15	0 90
60	63 12	2 94	9 88	1 13
70	65 10	2 00	9 40	1 07
80	66 69	1 38	8 81	1 16
90	67 99	0 94	8 21	1 27
100	69 03	0 62	7 67	1 26
120	70 63	0 29	6 61	1 29
140	71 85	0 13	5 64	1 51
160	72 8	0 06	4 80	1 76
200	74 29	0 03	3 36	1 68

Corrected final pressure taken as 77 7 cm k_2 for acetaldehyde at 509°C (Hinshelwood and Hutchison) = 4 37 × 10^{-3} cm $^{-1}$ min $^{-1}$

The values of k_2 show a marked decrease during the initial stages of the reaction and then remain fairly constant. The method involves uncertainties in the assumption that 65 per cent of the ether decomposes to acetaldehyde, and in the effects of the condensation reaction and the formation of ethylene. The value of k_1 may be in error to some extent, and there is the difficulty of obtaining slopes graphically of sufficient accuracy to give reliable results when relatively small differences have to be taken. In view of all this, the conclusions as to mechanism would seem to be fairly well justified by the agreement shown.

The mechanism here outlined involves the assumption that the temperature coefficient of the ether decomposition reaction is considerably larger than that for the aldehyde. The value of E, the critical increment for acetaldehyde, is 45,500 calories per mole, while for the decomposition of methyl ethyl ether, Glass and Hinshelwood give a value of 47,000 calories. Since the results given here are in definite disagreement with the results of these two authors with regard to the magnitude of the rates themselves, it is to be expected that the value of the temperature coefficient will also differ. The rate constants obtained here lead to a value of E of 65,300 calories per mole. Although, owing to the uncertainties entering into the method of treatment, this figure may be somewhat in error, E is apparently much larger than that given by Glass and Hinshelwood.

TABLE 8

Decomposition of the ether at 565°C.

Initial pressure, 28.7 cm.; k_1 = 0 603 min.$^{-1}$

t	P	P_e	b	$k_2 \times 10^2$
minutes	*cm*	*cm*	*cm*	*cm* $^{-1}$ *min.* $^{-1}$
0	28 7	28 7	0	
1	40 8	15 7	8 35	1 35
2	52 1	8 59	8 15	1 49
3	56 7	4 70	9 62	1 21
4	59 85	2 57	9 79	1 19
5	61 95	1 41	9 51	1 03
6	63 4	0 77	8 95	1 04
7	64 5	0 42	8 49	1 07
8	65 4	0 23	7 89	1 23
9	66 15	0 13	7 30	1 18
10	66 8	0 07	6 74	1 12
15	68 8	0 003	4 85	1 06
20	69 7	0 0002	3 95	0 64

The above value is consistent with the results obtained at the highest temperature, 565°C., as is shown in table 8. Here equation 4 may not be relied upon to obtain k_1, since the decomposition of the aldehyde is appreciable even near the start. k_1 was therefore obtained by extrapolation using the temperature coefficient. Values of b and k_2 were obtained using equations 1 and 3 as in table 7 The column headed P_e shows the pressure of undecomposed ether present at the times given, as calculated from the value of k_1. The agreement between the bimolecular constant obtained here and that in table 6 is quite good.

SUMMARY

1. The decomposition of methyl ethyl ether has been studied over a wide range of temperature and is shown to be a complex process consisting in the main of a unimolecular decomposition of the ether into acetaldehyde and methane, followed by the bimolecular decomposition of the acetaldehyde.

2. These two steps may be treated separately at high and low temperatures, owing to the difference in the two temperature coefficients.

3. A method of treatment of the process at intermediate temperatures has been developed, and values of the rate constants at various temperatures have been obtained.

REFERENCES

(1) Rice and Ramsperger: J. Am. Chem. Soc. **49**, 1617 (1927).
Kassel: J. Phys. Chem. **32**, 225 (1928).
(2) See Trans. Faraday Soc. **17**, 545 (1921), for a general discussion of this hypothesis.
(3) Ure and Tolman: J. Am. Chem. Soc. **51**, 974 (1929).
(4) Clusius and Hinshelwood: Proc. Roy. Soc. London **128A**, 82 (1930).
(5) Glass and Hinshelwood: J. Chem. Soc. **1929**, 1804.
(6) Williamson: Ann. **81**, 77 (1852).
(7) Mulliken: Identification of Pure Organic Compounds, Vol. I. Wiley and Sons, Inc., New York (1904).
(8) Allen: Commercial Organic Analysis, Vol. I, p. 327. P. Blakiston's Sons and Co., Philadelphia (1923).
(9) Pease: J. Am. Chem. Soc. **54**, 1876 (1932).
(10) Hinshelwood and Hutchison: Proc. Roy. Soc. London **111A**, 380 (1926)

ON THE MECHANISM OF GASEOUS REACTIONS. II

Homogeneous Catalysis in the Decomposition of Methyl Ethyl Ether

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During the course of a series of experiments on the thermal decomposition of methyl ethyl ether, some anomalies were observed in the measured rates where different preparations of the ether were used (1). Under the same conditions of temperature and pressure different samples of the gas showed widely different rates. It was suspected that the presence of some impurity in varying amounts was producing a catalytic effect. Since the ether was prepared from sodium methoxide and ethyl iodide, a likely impurity in the product would be the latter substance, and in some of the experiments a brownish deposit, probably iodine, was observed in the capillary tubing above the furnace enclosing the reaction flask. Clusius and Hinshelwood have shown that the alkyl iodides will produce homogeneous catalysis in the case of the decomposition of several ethers, the catalytic effect being largely due to iodine vapor formed by the decomposition of the halide (2).

Since it was desired to study the decomposition of methyl ethyl ether in absence of catalysts, the method of preparation was modified in such a way as to ensure the virtual absence of any iodide in the product. The results of this work have been given in the previous communication of this series.

A few experiments have been carried out for the purpose of substantiating the conclusion that the observed discrepancies in rates were due to catalysis by the alkyl halide, and these are reported here. The results of some calculations as to the mechanism of the catalytic process are also given, since, as in the case of the uncatalyzed decomposition, consecutive reactions appear to be involved.

EXPERIMENTAL

The apparatus employed was the same as that used in the previous work except for the addition of a small bulb containing ethyl iodide. In carrying out a rate measurement a small quantity of ethyl iodide vapor was first admitted to the hot reaction chamber, and heated for a few minutes before the sample of ether was introduced. This should ensure complete decomposition of the iodide at these temperatures (2). Since in previous experiments where catalysis was suspected, the residual gas after decomposition showed approximately the same composition as that obtained in the uncatalyzed process, the gas mixture from the experiments in which ethyl iodide was added was not analyzed, and it was assumed that the reactions taking place were substantially the same as those in the previous cases.

RESULTS

The effect of the addition of ethyl iodide is to produce a marked increase in rate, as may be seen from the values given in table 1. In fact, in run 33 where the highest concentration of iodide was used, the pressure increase was so rapid that it was impossible to obtain pressure readings until the reaction was substantially complete. In the table t_{50} represents the time in minutes for the pressure increase to reach one-half of its final value, and in the case of a single unimolecular reaction these values would be inversely proportional to the reaction rate constant. The reactions here are more complex, nevertheless the time values give an approximate idea of relative rates. Run No. 25 shows the time for the uncatalyzed reaction. The same preparation of ether (sample 5) was used in all of these experiments. The fourth column gives the pressure in the reaction chamber just before the ether was admitted, this being due to the decomposition products of ethyl iodide. Since the connecting tubes outside the furnace were not heated some iodine would condense in these, as was observed in run 33. For this reason the concentrations of catalysts cannot be accurately compared. However it is evident from run 35 that even a small quantity of iodide produces a considerable acceleration.

TABLE 1

The effect of ethyl iodide upon the rate of decomposition of methyl ethyl ether

NO.	TEMPERATURE	INITIAL PRESSURE	PRESSURE DUE TO IODIDE	t_{50}
	degrees C	*cm*	*cm*	*minutes*
25	487	24 96	0	66 7
33	487	11 4	9 1	(0 5)
34	487	24 1	2 5	1 14
35	480	26 95	0 06	9 17

In table 2 are given the time values for experiments carried out with several preparations of ether at various temperatures, showing the great differences obtained. The effect of the variation of the initial pressure (and consequent variation in the concentration of the catalyst) is well shown in the second and third lines where a decrease in pressure to one-fifth of its value decreases the rate approximately three times. The time values for sample 5 represent the rates for the uncatalyzed process, since it is believed that this preparation of ether was virtually free from iodide. The last line refers to one of the experiments (run 35) in which iodide was added.

The effect of increasing the surface exposed in the reaction tube was rather unexpected. With the tube packed with glass wool, a *decrease* in rate was observed, and the course of the reaction was no longer even approximately unimolecular, as shown by the values of t_{25}, t_{50}, and t_{75} (table 3, previous paper). In the presence of Pyrex rods a similar decrease was noted, but in a lesser degree. The explanation of these results is possibly that of adsorption of iodide or iodine on the surface with reduction in its catalytic activity.

TABLE 2

Time values for experiments with different samples of methyl ethyl ether at various temperatures

SAMPLE OF ETHER	INITIAL PRESSURE	t_{50}			
		at 456–7°C	at 486–7°C	at 509–10°C	at 561–5°C
	cm.	*minutes*	*minutes*	*minutes*	*minutes*
2	8 and 12			18 9	2 1
3	14 and 17		5 6	2 1	
3	3 2		15 9		
3	15			30 6*	
3	15 and 20		13 5†	7 4†	
4	10 3	29 5			
5	25 to 30	377 6	66 7	34 3	2 2
5	27	9 17 (480°C.)‡			

* In presence of glass wool.

† In presence of Pyrex rods.

‡ Ethyl iodide introduced to a pressure of about 0 06 cm.

The various samples of ether were prepared from the same reagents. The values in table 2 indicate that in ether sample 2 the concentration of iodide was lower than in sample 3. This was to be expected, since in the preparation of sample 2 a smaller proportion of iodide was used in comparison with the sodium methoxide. The chief difference in the method used for sample 5 was in connection with the time allowed. The reaction mixture of methoxide and iodide consists of two layers with the heavy iodide forming the lower. The reaction at the interface is rather slow unless the temperature is raised to such a value that there is danger of the reagent distilling over. In the preparation of sample 5, the mixture was allowed to stand at room temperature until the lower layer had completely disappeared, a matter of six days, after which treatments with sodium and several careful fractionations were carried out. The results seem to point unmistakably to the presence of iodide in the other preparations.

THE KINETICS OF THE CATALYTIC PROCESS

Clusius and Hinshelwood (3) have shown that the decomposition of acetaldehyde catalyzed by iodine follows a unimolecular course with respect to the aldehyde itself, and that the catalytic decomposition of ethyl ether consists of consecutive unimolecular reactions. The same state of affairs is to be expected in the present case, in which a large proportion of the methyl ethyl ether decomposes into acetaldehyde and methane.

The treatment of the experimental results is somewhat simpler than that given for the uncatalyzed process (1). Here a solution of the differential equations is possible, but it is easier to retain the differential form in treating the data.

The value of k_1, the rate constant for the ether, may be obtained as in the previous case or may be estimated from the slope of the pressure–time curve at the origin.

The equation for k_2', the unimolecular constant for acetaldehyde, becomes

$$\frac{dP}{dt} = k_1 (P_f - 1.65 P_i) e^{-k_1 t} + k_2' b$$

where as before $\frac{dP}{dt}$ is the slope at time t of the curve obtained by plotting the total pressure throughout decomposition against the time. P_f and P_i are the final and the initial pressures respectively, and b is the partial pressure of acetaldehyde at time t.

In table 3 is shown the results of applying this method to an experiment at 480°C., in which 26.95 cm. of ether from sample 5 were used in the presence of ethyl iodide, the pressure due to the catalyst being about 0.06 cm. There is some doubt as to the correct value of k_1, since k_2' is relatively large and the decomposition of the acetaldehyde is taking place at an appreciable rate even at the start. The values of b show the expected rise and fall and values of k_2' for a unimolecular process given in the fourth column show fair agreement up to a time of 20 minutes, after which both b and the pressure of the ether become small. In the last column are shown values calculated for a bimolecular reaction on the part of the acetaldehyde and the variation is much larger than for the unimolecular case. In table 4 the same treatment is applied to an experiment at 456°C. in which 10.25 cm. of ether from preparation 6 was used without further addition of catalyst. Here the agreement in the values of k_2' in column four is quite satisfactory.

As in the uncatalyzed decomposition, the analyses indicate a part of the ether forms formaldehyde and ethane, followed by the rapid decomposition

TABLE 3

Experiment on ether sample 5 and ethyl iodide at 480°C.

$k_1 = 0.146 \text{ min.}^{-1}$

t	P	b	k_2' (uni)	k_2 (bi)
minutes	*cm*	*cm*		
0	26 95	0		
1	30 15	2 75	0 131	0 048
2	33 15	4 75	0 135	0 028
3	36 05	6 25	0 126	0 020
4	38 85	7 15	0 130	0 018
5	41 45	7 95	0 116	0 015
6	43 85	8 25	0 121	0 015
7	46 15	8 45	0 113	0 013
8	48 05	8 65	0 110	0 013
9	49 9	8 60	0 102	0 012
10	51 5	8 60	0 091	0 011
20	62 3	5 47	0 111	0 020
30	66 7	2 84	0 086	0 030
40	68 5	1 47	0 068	0 046

TABLE 4

Experiment on ether sample 4 at 456°C.

$k_1 = 0\ 030 \text{ min}^{-1}$

t	P	b	k_2' (uni)	k_2 (bi)
minutes	*cm*	*cm*		
0	10 25	0		
10	13 45	1 34	0 034	0 025
20	15 98	2 16	0 029	0 013
30	18 10	2 52	0 025	0 0099
40	19 85	2 60	0 025	0 0096
50	21 25	2 56	0 023	0 0090
60	22 37	2 45	0 022	0 0090
70	23 30	2 27	0 024	0 011
80	24 20	1 92	0 027	0 014
90	24 98	1 55	0 031	0 020
100	25 60	1 23	0 033	0 027
110	26 03	1 03	0 025	0 024
120	26 35	0 87	0 026	0 030
150	27 00	0 51	0 030	0 059
			Av. =0.027	

of the formaldehyde, and the slow decomposition of a part of the ethane to an equilibrium with ethylene and hydrogen. In the former case the ethane decomposition was found to be relatively slow and heating for a day or two was usually required to reach a constant pressure. Thus in an experiment

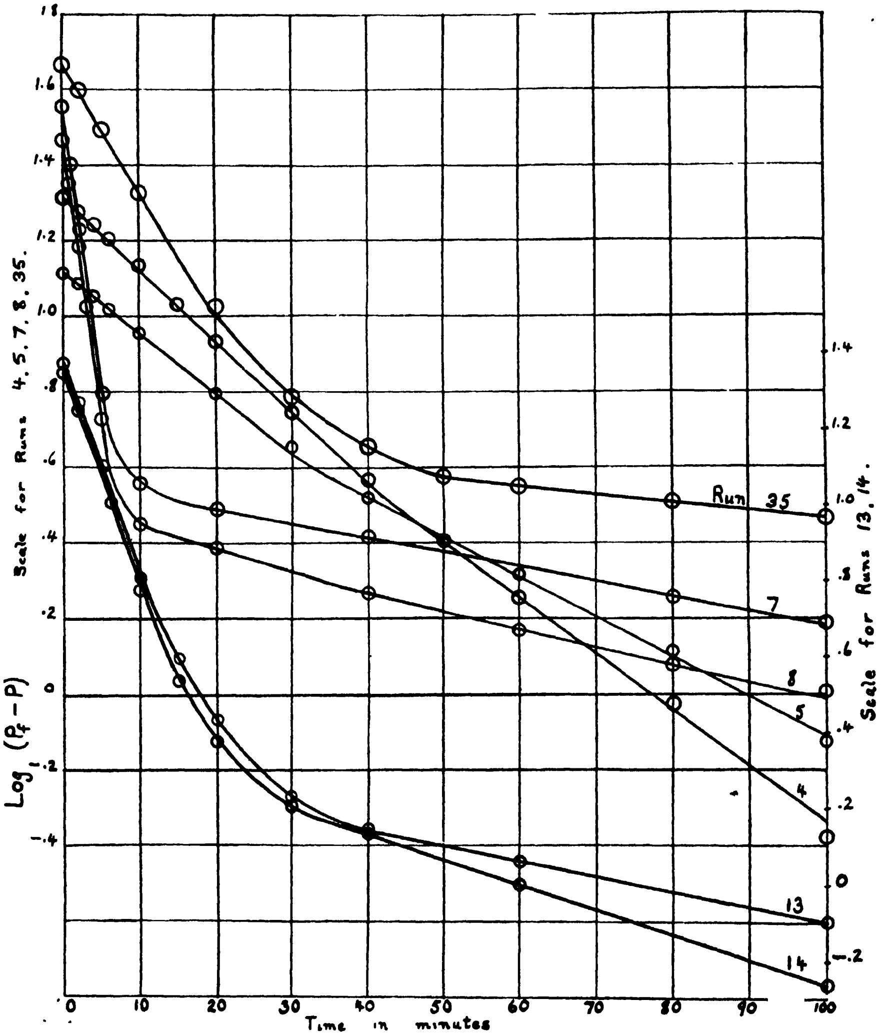

Fig. 1

RUN NO.	TEMPERATURE	INITIAL PRESSURE	ETHER SAMPLE
	degrees C.	*cm.*	
4	503	11.9	2
5	509	7.7	2
7	510	21.0	3
8	510	17.3	3
13	487	14.1	3
14	487	13.4	3
35	480	26.95	5 + ethyl iodide

at 565°C. an approximate calculation based on the pressure rise after 50 minutes gave for a unimolecular constant 3.4×10^{-3} min.$^{-1}$, while from the work of Marek and McCluer (4) the constant for ethane decomposition is calculated to be 8.9×10^{-3} min.$^{-1}$

In the catalytic experiments in most cases there was noted a slow rise in pressure following the first relatively rapid increase. Moreover if a logarithmic plot is made, the lines appear to show two main slopes. This is illustrated in figure 1 in which are plotted the values of log $(P_f - P)$ against the time for a number of the catalytic runs. P is the total pressure at any time, and P_f the final total pressure. If the process was a simple unimolecular one such a plot would produce a straight line. In the figure it is shown that in most cases the lines are approximately straight in the first portion of any run; then there is a rapid change of slope to a much lower value.

The first part of the plot evidently refers to the decomposition of ether followed by that of acetaldehyde, and corresponds approximately to a single unimolecular process, since k_1 and k_2' are close together in value, as shown in tables 3 and 4. That the second slope corresponds to the decomposition of ethane seems a reasonable assumption, since the rate is too slow for that of acetaldehyde, and moreover the amount of pressure change during the second stage is of the right order of magnitude as calculated from the equilibrium data for the reaction

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 \tag{5}$$

In the case of runs 4 and 5 (and some others not shown here), the initial rates are slow and the experiments were not carried on long enough to reach the equilibrium pressure.

The experimental data for this final stage in the decomposition process is not sufficiently accurate to provide reliable values of the unimolecular constant for ethane, but approximate calculations indicate considerably higher values than would be expected at the temperatures used. This points to catalysis also in the decomposition of the ethane.

It is to be noted that at the temperatures at which the catalytic reactions were carried out, the uncatalyzed reactions were also taking place at measurable rates, as shown in the previous paper, although in most cases the effect of the latter should be negligible.

SUMMARY

1. The decomposition of methyl ethyl ether is catalyzed in the presence of small quantities of ethyl iodide such as may remain in the ether as a result of its preparation.
2. The catalytic process consists mainly of the unimolecular decompo-

sition of the ether followed by the unimolecular decomposition of the acetaldehyde formed.

3. Ethane seems also to be a primary product and the decomposition to an equilibrium mixture with ethylene and hydrogen is catalyzed as a result of the iodide.

REFERENCES

(1) Ure and Young: J. Phys. Chem. **37**, 1169 (1933).
(2) Clusius and Hinshelwood: Proc. Roy. Soc. London **128A**, 75 (1930).
(3) Reference 2, pp. 82 and 88.
(4) Marek and McCluer: Ind. Eng. Chem. **23**, 878 (1931).
(5) Pease: J. Am. Chem. Soc. **54**, 1876 (1932).

THE PARTIAL PRESSURES OF WATER IN EQUILIBRIUM WITH AQUEOUS SOLUTIONS OF SULFURIC ACID[1]

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In connection with a method developed by Collins and Menzies for measuring aqueous tensions in salt hydrate systems, which is to be described in a subsequent paper, a knowledge was required of the partial pressures of water over aqueous solutions of sulfuric acid for various concentrations and at various temperatures. Critical discussions of existing data have been given by Wilson (1), Greenewalt (2), and Hepburn (3), and tables have been compiled. The agreement between their values at 25°C. indicates that this isotherm is fairly accurately located. At other temperatures, however, the tables of Wilson and Greenewalt do not agree to the extent expected if the claims of accuracy of each are considered, the disagreement in many cases being more than 4 per cent. We decided, therefore, to redetermine experimentally the vapor pressures over aqueous solutions of sulfuric acid.

CHOICE OF METHOD

The dynamic boiling point method employed by Burt (4) presents many difficulties. Among the principal objections are superheating, change of concentration with boiling, and the existence of a pressure gradient. The gas-current saturation method used by Briggs (5), Sorel (6), and others presents difficulties in temperature control and is accompanied by a change in concentration of the solution. The dew point method used by Hepburn (3) is practical for only moderate temperatures. The static methods used by Regnault (7), Brönsted (8), Dieterici (9), Grollman and Frazer (10), and Hacker (11), permit greater accuracy. A static method was therefore desirable. The method chosen consisted of a modification of the static isoteniscope of Smith and Menzies (12). The partial pressure of hydrogen sulfate or sulfur trioxide over aqueous sulfuric acid solutions is not appreciable below 150°C. According to Thomas and Barker (13) the partial pressure of hydrogen sulfate over a 99 per cent solution is 0.5 mm. at 180°C. Hence a method measuring the total vapor pressure of a solution will, in effect, give results for the aqueous partial pressure.

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[1] From a thesis presented by the author to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

Isoteniscope

For details of the static isoteniscope one is referred to the original article (12). The static isoteniscope as described there is applicable in the case of single substances and saturated solutions. It is, however, not directly applicable in measuring vapor pressures of liquid pairs or unsaturated solutions. In these cases the repeated boiling-out to insure the expulsion of all the dissolved or absorbed foreign gases would be followed by a change in the concentration of the solution. It was necessary to devise an isoteniscope which would permit the expulsion of the foreign gases with no accompanying change in concentration. Jacketing the part of the isoteniscope nearest the manometer with a water condenser would prevent loss

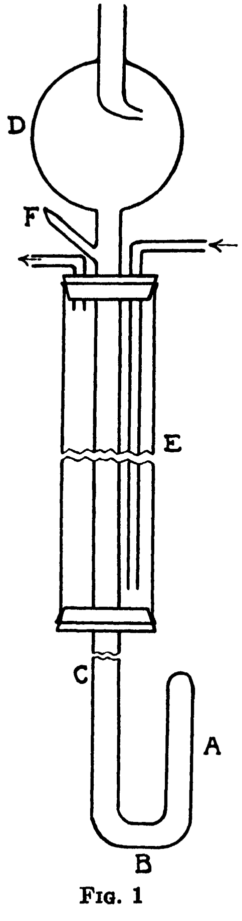

FIG. 1

of water from the instrument itself, but the solution in the bulb would become more concentrated, while the solution acting as the confining liquid would become more dilute on account of the returned condensed water vapor. This difficulty was obviated by abbreviating the instrument to a J-tube (figure 1). It was made from glass tubing (7 mm. internal diameter). The closed end, A, was approximately 6 cm. long and the length over all was 40 cm. The water jacket, E, was constructed from 20-mm. tubing and was fitted to the isoteniscope with rubber stoppers. The condenser was put in place before sealing on the Kjeldahl trap D. It proved convenient to have both the inlet and outlet tubes of the condenser inserted through the top stopper. The Kjeldahl trap was added as a safety device to protect the pressure measuring system from an influx of acid solution should the pressure in the isoteniscope accidentally become much larger than the applied pressure. The side tube, F, which may be opened or sealed at will, permits greater facility in washing and charging.

Since approximately 5 cc. of solution were needed there arose the question of a change in concentration through the possibility of condensed water in part C at times other than during the process of air removal. On no occasion was any water ever observed laving the inner walls of the condenser, so that the amount of water must have been small. And yet no vapor escaped past the condenser, which was proven by the subsequent analysis of several samples of acid solutions after having been used in the pressure determinations from 25°C. to the vicinity of 125°C., the concentration agreeing with the initial concentration within the experimental error. To get an idea how small an amount of water, if any, was on the walls of the condenser the following experiment was performed. The glass tubing between the isoteniscope proper and the condenser was bent so that it was approximately 70° from the vertical and the condenser 20° from the vertical. A piece of glass tubing several centimeters long and having a closed end was sealed to the underside just below the condenser forming an "appendix." The isoteniscope was charged with an acid solution with a boiling point of approximately 110°C. and connected with the pressure measuring system. The isoteniscope proper was maintained at 105°C. and the pressure in the system adjusted accordingly. The "appendix" was kept cold by immersion in a bath of water. At the end of two hours the "appendix" was cut off and its water content determined. The water which collected was inappreciable, i.e., less than 0.01 g., an amount having too small an effect upon the concentration to cause concern. This may not seem surprising when we stop to consider that the only way for the water to reach the condenser was by diffusion through a tube 14 cm. long and of 7 mm. diameter against an opposing equal pressure of air, except during the process of air removal.

Preparation of solutions

The acid solutions used in these determinations were prepared from redistilled sulfuric acid of the best reagent grade. An analysis of the acid was made, which showed that the statement made by the manufacturer regarding the maximum limits of impurities was correct. This statement showed that the acid conformed to the standards of purity as given by Murray (14). The various solutions were analyzed in triplicate for sulfate by precipitating and weighing as barium sulfate. The analyses checked within 0.04 of a percentage of composition, which amounts to an error of less than 0.1 per cent for most of the solutions.

Temperature regulation

For the lower temperatures a water-bath consisting of a 4-liter beaker was used; for the higher temperatures oil was substituted for the water. The bath was jacketed with an inch of asbestos, the variety commonly used for wrapping steam pipes. The temperature was regulated by an electric hot-plate in series with a variable resistance. An additional electric heater of the immersion type was used to facilitate raising the temperature rapidly and then disconnected when the desired temperature was reached. A coil of copper tubing immersed in the bath, through which cold water could be run, afforded the means of cooling when necessary to lower the temperature. The temperature was controlled within 0.01 to 0.02°C. Violent stirring was provided and uniformity of temperature throughout the bath was obtained.

Thermometry

The temperature was measured by means of a platinum resistance thermometer of the Callendar type with compensating leads. The platinum wire was wound on a mica form and was jacketed with a porcelain tube. It was calibrated at the freezing and boiling points of water and at the transition point of sodium sulfate decahydrate.

Resistances were measured by means of a Mueller type thermometer bridge (15). The makers supplied calibration data showing no deviations which would affect our results. The sensitivity of the galvanometer was such that a change in the resistance of the thermometer of 0.001 ohms, corresponding to 0.01°C., produced a deflection of one half a scale division. No thermal E.M.F. causing more than 0.01°C. was observed. The fixed points showed no change throughout the period of the measurements, probably because the thermometer was never heated above 140°C.

Pressure

The manometer was similar to the one described by Smith and Menzies (12). The mercury was purified by the nitric acid treatment and subsequent distillation *in vacuo*. The manometer levels were measured by a graduated steel bar, the length of which was calibrated by comparison with a standard meter, the latter having been calibrated by the late Dr. E. W. Morley. The graduations were compared by means of dividers for 5 cm. intervals. There were no discrepancies large enough to affect our results. The room temperature variation was so small that the bar was not noticeably affected. The steel bar carried a movable sleeve with a vernier scale. To this sleeve was attached a strip of mirrored glass with a horizontal hair line, in such a way that it was behind the manometer tubes on each side of the steel bar. The hair line could be adjusted at the mercury level, avoiding parallax by the alignment of the mercury level with its image. The manometer readings were reduced to millimeters of mercury at 0°C. and to sea level at 45° N.L. The value of the gravity constant, g, was taken as 980.3, the calculated value for Williamstown, Mass., according to its latitude, longitude, and elevation. This value agrees with that determined in the Thompson Physical Laboratory of Williams College.

For pressures less than one atmosphere the "open end" of the manometer was connected to a system containing a Hyvac pump and McLeod gauge. This system was evacuated to a residual pressure of 0.005 mm., thereby obviating the reading of the barometer at each determination and also increasing the accuracy of the measurements.

Pressures less than 10 mm. were read by means of another McLeod gauge protected from water vapor by a guard tube containing magnesium perchlorate trihydrate.

Since an open-end manometer was used for pressures above one atmosphere the barometer had to be read. The barometer was by Henry Green of Brooklyn, N.Y. It was tested for accuracy by comparison with the manometer when the open end was at atmospheric pressure. The Green barometer was found to be accurate within the error of reading the instruments.

Manipulation

The essential difference in the manipulation of this isoteniscope and that of Smith and Menzies was the method by which the dissolved gases were removed. Enough solution was placed in the isoteniscope to fill the closed arm about one-half full when the levels of the solution in both arms were equal. About 5 cc. were required. Then the isoteniscope was connected to the system and the latter evacuated. Bubbles of gas were given off from the solution and part of this gas collected in the closed end of the isoteniscope. This was removed from time to time by bringing the instrument to horizontal position. Sharp tapping aided in the removal of the gas from the solution. After several repetitions of gas removal it was necessary to warm gently the closed end of the instrument in order to form a bubble of water vapor. If the isoteniscope was swung quickly back and forth through a small arc, as a clock pendulum, a sharp click was heard when the solution struck the closed end. This was an index of the absence of foreign gases. As further proof of the removal of gases a measurement of the aqueous tension was made at a given temperature and then the process of gas removal repeated at a higher temperature. A redetermination of the pressure at the first temperature was then repeated and identical values ensured the absence of all foreign gases. Any water which might have deposited in the condenser during the process of air removal was allowed sufficient time to reflux and become thoroughly mixed with the solution before the pressure measurements were made.

EXPERIMENTAL RESULTS

The experimental results are given in table 1.

FINAL TABULATION OF RESULTS

Since the vapor pressures measured were for solutions of various concentrations and at various temperatures it was necessary to devise a method whereby the aqueous tensions of solutions of intermediate concentrations could be obtained at any desired temperature.

The experimental data was first smoothed by a highly sensitive graphical method. In this method the log of the pressure is temporarily assumed to be a linear function of the reciprocal of the absolute temperature. Since log P, however, is not strictly a linear function of $1/T$ there was a difference between the logs of the observed pressures and those so calculated. These differences were plotted as a function of temperature, and by their aid the pressures at rounded temperatures were calculated for intervals of 5°C.

Since the relative vapor pressure for a solution changes only slowly with temperature, graphs showing this relation allowed us to test the data smoothed as above and to smooth it further where necessary. Extrapolation of these curves gave the values for 20°C., 140°C., and in some cases 135°C.

The relative vapor pressures for solutions of rounded concentrations were next obtained graphically. To accomplish this, the logs of the smoothed relative vapor pressures were plotted as a function of the concentration. Although no experimental data was obtained for concentrations below 29.90 per cent the extrapolation of the isotherms from this concentration to 0 per cent was accomplished without the introduction of appreciable error. The logs of the relative vapor pressures for 10 per cent, 20 per cent, and 25 per cent were read directly from these isotherms. Instead of obtaining the logs of the relative vapor pressures for solutions above and including 30 per cent directly from the graphs, we obtained them by a more accurate method. This method involved calculating them on the temporary assumption of a parabolic relation between the log of the relative vapor pres-

TABLE 1

Vapor pressure for sulfuric acid–water solutions

Experimental concentrations. Pressure in millimeters of mercury

t	*P* (OBSERVED)	*t*	*P* (OBSERVED)	*t*	*P* (OBSERVED)	*t*	*P* (OBSERVED)
29.90 per cent H_2SO_4							
degrees C		*degrees C*		*degrees C*		*degrees C*	
24 87	17 8	39 69	41 1	69 85	179 0	99 71	590 7
24 41	17 0	44 90	54 5	74 83	221 1	104 44	699 2
30 00	24 1	49 71	69 6	79 67	270 7	110 06	845 1
29 90	23 7	54 91	89 9	85 32	341 9	113 85	964 4
34 45	30 7	59 72	112 9	89 92	408 1	119 33	1155
34 40	31 0	64 59	141 7	94 78	491 0	123 06	1296
38 23 per cent H_2SO_4							
25 82	15 0	57 32	82 4	90 67	351 5		
31 44	21 1	63 11	108 4	96 51	440 3		
36 20	27 5	69 69	146 5	103 13	561 1		
45 88	46 3	76 29	195 4	110 80	737 7		
50 51	59 2	82 71	255 4	123 64	1133		
55 44	74 8	86 09	292 1	129 25	1344		
43 36 per cent H_2SO_4							
25 20	12 0	54 17	59 2	84 39	231 6	115 56	743 3
29 95	15 6	59 12	75 6	90 16	293 9	119 16	844 9
36 53	23.2	64 75	97 7	94 86	353 1	124 25	996 4
39 99	28 0	69 76	123 7	99 73	423 0		
44 67	36 2	74 79	154 3	104 76	511 9		
49 72	47 0	79 98	193 0	109 92	614 8		
48 12 per cent H_2SO_4							
26 04	10 1	61 60	69 8	94 75	296 1	129 11	990 7
32 81	14 9	69 83	102 4	99 23	349 3		
41 61	24 9	74 53	126 4	104 81	430 3		
46 58	32 4	80 04	160 8	109 64	513 6		
51 18	41 5	84 19	191 8	114 26	602 7		
55 29	51 0	89 41	237 5	121 27	766 1		
52 68 per cent H_2SO_4							
24 49	7 01	54 29	37 9	85 05	159 8	115 53	523 0
29 69	9 60	59 40	49 4	90 29	199 9	119 75	601.2
34 48	13 0	64 57	63 6	94 96	239 8	125 98	750 6
39 93	17 4	70 17	83 4	100 43	298 5		
44 50	22 4	74 42	102 2	105 37	361.2		
50 15	30 7	79 65	127 0	109 20	412 8		

TABLE 1—*Concluded*

t	*P* (OBSERVED)	*t*	*P* (OBSERVED)	*t*	*P* (OBSERVED)	*t*	*P* (OBSERVED)
58 03 per cent H_2SO_4							
degrees C.		*degrees C*		*degrees C*		*degrees C.*	
25 11	4 82	59 95	35 5	89 87	139 5	120.74	453.2
33 95	8 40	65 01	45 6	95 06	172 9	125 42	533.8
40 58	12 4	70 13	58 3	100 15	211 1	130 20	630.0
45 05	16 1	74 95	72 7	104 10	246 2	135 61	752 8
49 77	20 1	80 22	92 2	109 66	303 9		
55 19	28 0	85 16	114 3	114 99	370 1		
65 47 per cent H_2SO_4							
29 72	2.89	59.98	18 02	90 16	77 4	119.13	247.8
34 99	4 29	64 36	22.7	94 71	93.9	124.41	301 2
39 59	5 37	69 86	29.8	100 20	118 5	129 46	361 1
44 66	7 58	74 52	37 6	104 56	141 3		
49 77	10.16	79 19	46 9	109 96	174 9		
54 91	13 74	84 72	60 6	114 74	210 6		

sure and the concentration, a method similar to the one described above where a linear function was temporarily assumed.

Table 2 presents the final tabulation of the relative vapor pressures. The first and second columns, respectively, give the temperature and the vapor pressure of water in millimeters of mercury. The other columns give the relative vapor pressures in per cent for the solutions designated at the head of each column. Values for intermediate concentrations and temperatures may be obtained by linear interpolation from table 2 without introduction of large errors, since the R.V.P. isotherms are sufficiently rectilinear for intervals of 10 per cent and the relative vapor pressure for a solution of given concentration is a linear function of the temperature. Relative vapor pressures at temperatures not far above 140°C. may be obtained by linear extrapolation. Values in table 2 for 145°C. and 150°C. have been so obtained.

ACCURACY OF RESULTS

The maximum absolute error in temperature measurement we estimate at 0.05°C. For our most dilute solution this could cause an error of 0.1 per cent at 125°C. and 1 per cent at 25°C. From a study of the smoothing required of our results we find that the average smoothing required below 10 mm. amounts to 1.5 per cent. Between 10 mm. and 100 mm. the average smoothing amounts to 0.2 per cent. Above 100 mm. it amounts to but 0.1 per cent. In terms of pressure this would correspond to an average better than 0.15 mm. below 10 mm., and 0.2 mm. above 10 mm. This error corresponds to the limit of error in reading the manometer, McLeod gauges, and barometer.

Since the pressures for 10 per cent, 20 per cent, and 25 per cent were obtained by graphic interpolation of the logs of the relative vapor pressures, their accuracy depends upon the accuracy with which the isotherms of log R.V.P. versus concentration were located when they were extrapolated to zero concentration. We estimate that the probable error involved when reading the log of R.V.P. from these isotherms is not more than 0.005 units, which introduces approximately 1 per cent error in the relative and absolute

TABLE 2

Relative vapor pressures for sulfuric acid–water solutions

t	*P* (FOR WATER)	RELATIVE VAPOR PRESSURES IN PER CENT FOR SOLUTIONS CONTAINING FROM 10 TO 70 PER CENT H_2SO_4											
		10 per cent	20 per cent	25 per cent	30 per cent	35 per cent	40 per cent	45 per cent	50 per cent	55 per cent	60 per cent	65 per cent	70 per cent
degrees C.	*mm.* Hg												
20	17.54	95.6	88.0	82.4	75.0	66.0	56.1	45.6	35.2	25.3	16.1	9.2	3.4
25	23.76	95.6	88.0	82.5	75.2	66.3	56.5	46.1	35.7	25.8	16.6	9.7	3.7
30	31.82	95.6	88.0	82.6	75.4	66.6	56.9	46.6	36.2	26.3	17.1	10.1	4.1
35	42.18	95.6	88.1	82.8	75.6	66.9	57.3	47.1	36.8	26.8	17.5	10.5	4.4
40	55.32	95.6	88.1	82.9	75.8	67.3	57.7	47.5	37.3	27.4	18.0	11.0	4.8
45	71.88	95.6	88.2	83.0	76.0	67.6	58.1	48.0	37.8	27.9	18.5	11.4	5.1
50	92.51	95.6	88.2	83.1	76.2	67.9	58.5	48.5	38.3	28.5	19.0	11.8	5.4
55	118.0	95.6	88.3	83.2	76.4	68.2	58.9	48.9	38.9	29.0	19.5	12.3	5.8
60	149.4	95.6	88.3	83.3	76.6	68.5	59.3	49.4	39.4	29.6	20.0	12.7	6.2
65	187.5	95.6	88.4	83.4	76.8	68.8	59.7	49.9	39.9	30.1	20.4	13.1	6.5
70	233.7	95.6	88.4	83.5	77.0	69.1	60.1	50.4	40.5	30.6	20.9	13.5	6.8
75	289.1	95.6	88.5	83.6	77.2	69.5	60.5	50.8	41.0	31.1	21.4	14.0	7.2
80	355.1	95.6	88.5	83.8	77.4	69.8	60.9	51.3	41.5	31.7	21.9	14.4	7.5
85	433.6	95.6	88.6	83.9	77.6	70.1	61.3	51.7	42.1	32.2	22.4	14.8	7.8
90	525.8	95.6	88.6	84.0	77.8	70.4	61.7	52.2	42.6	32.7	22.8	15.2	8.2
95	633.9	95.6	88.7	84.1	78.0	70.7	62.2	52.7	43.1	33.3	23.3	15.7	8.5
100	760.0	95.6	88.7	84.2	78.2	71.0	62.6	53.1	43.6	33.8	23.8	16.1	8.9
105	906.1	95.6	88.8	84.3	78.4	71.3	63.1	53.6	44.2	34.3	24.3	16.5	9.3
110	1075.	95.6	88.8	84.4	78.6	71.7	63.4	54.1	44.7	34.9	24.8	17.0	9.6
115	1268.	95.6	88.8	84.6	78.8	72.0	63.8	54.5	45.2	35.4	25.2	17.4	9.9
120	1489.	95.6	88.9	84.7	79.0	72.3	64.2	55.0	45.7	35.9	25.7	17.8	10.3
125	1741.	95.6	88.9	84.8	79.2	72.6	64.6	55.5	46.3	36.5	26.2	18.3	10.6
130	2026.	95.6	89.0	84.9	79.4	72.9	65.0	55.9	46.8	37.0	26.7	18.7	11.0
135	2347.	95.6	89.0	85.0	79.6	73.2	65.4	56.4	47.3	37.0	27.1	19.1	11.3
140	2710.	95.6	89.1	85.1	79.8	73.5	65.8	56.8	47.8	38.1	27.6	19.5	11.7
145	3117.	95.6	89.1	85.2	80.0	73.8	66.2	57.3	48.3	38.6	28.1	19.9	12.0
150	3570.	95.6	89.2	85.3	80.2	74.2	66.6	57.8	48.8	39.1	28.6	20.4	12.4

vapor pressures. For the concentrations from 30 per cent to 65 per cent whose relative vapor pressures were obtained as described, the probable error is not more than 0.3 per cent. Since the pressures for 70 per cent were obtained by extrapolation, their accuracy is probably not better than 1 per cent.

Table 3 compares our values at 25°C. with those of Hepburn, Wilson, and Greenewalt. A comparison with the values of Wilson and Greenewalt at higher temperatures seems to show better agreement between our values and those of Greenewalt, although in many instances our values are intermediate between those of Wilson and Greenewalt.

TABLE 3

Comparative 25° isotherm

Rounded concentrations Pressures in millimeters of mercury

SULFURIC ACID	OUR VALUES	VALUES OF WILSON	VALUES OF GREENEWALT	VALUES OF HEPBURN
per cent				
10	22.7	22.8	22.4	22.7*
20	20.9	21.0	20.8	20.9*
25	19.6	19.7	19.4	19.6*
30	17.9	17.9	17.8	17.8
35	15.8	15.8	15.8	15.8
40	13.4	13.5	13.5	13.4
45	11.0	11.1	10.9	10.9
50	8.48	8.7	8.45	8.36
55	6.13	6.3	6.15	6.05
60	3.94	4.1	3.97	3.95
65	2.30	2.3	2.24	2.14
70	0.88	1.2	1.03	0.88
75		0.55	0.41	0.41
80		0.19	0.12	0.13

* Agree with the values obtained from the data of Grollman and Frazer (10).

RELATED THERMAL DATA

The heat of vaporization of water from an aqueous solution of sulfuric acid may be calculated from our vapor pressure data by the aid of the Clausius-Clapeyron equation in its approximate form

$$\frac{d \ln P}{dT} = \frac{Q}{RT^2} \tag{1}$$

Here Q is the heat absorbed in the evaporation of one mole of water from a large amount of solution so that there is no accompanying change in concentration. This is equal to the heat effects involved in removing one mole of liquid water from the solution and evaporating it. If we assume Q to be constant, we may integrate and obtain the equation:

$$\log P = \frac{Q}{2.3\ RT} + B \tag{2}$$

Upon plotting log P versus $1/T$ we obtain a line whose slope is $\frac{Q}{2.3R}$. The heat of vaporization, however, and in consequence the slope, is known to decrease with increasing temperature, attaining the value zero at the critical temperature.

The graphs of our results showed that the slopes of these curves were functions of the concentration as well as the temperature. The slope and the heat of vaporization increase with the concentration of sulfuric acid, since more work is required to remove water from a solution of greater concentration (cf. Greenewalt 2) The heat of vaporization at a given temperature could be calculated from the slope at that temperature. Since, however, the slope changes with temperature, it is best that there be chosen a small temperature interval to obtain the slope from the ratio $\frac{\Delta \log P}{\Delta 1/T}$. The values of $\Delta \log P$ and $\Delta 1/T$, however, can be made necessarily small only at the sacrifice of the accuracy of the ratio.

TABLE 4

Heats of vaporization for sulfuric acid-water solutions

Q (calories per gram) = $A\ t°\text{C} + B$

	WATER	10 PER CENT	20 PER CENT	25 PER CENT	30 PER CENT	35 PER CENT	40 PER CENT	45 PER CENT	50 PER CENT	55 PER CENT	60 PER CENT	65 PER CENT	70 PER CENT
A	− 61	− 61	− 61	− 61	− 61	− 61	− 61	− 61	− 61	− 61	− 61	− 68	− 95
B.	597	597	599	601	604	610	618	626	634	644	655	690	754

In order to avoid this difficulty the method of calculating the heats of vaporization was modified Since Q is a function of the rate of change of log P with $1/T$ it follows that for two substances the ratio of the heats of vaporization at a given temperature is equal to the ratio of their rates of change of log P at that temperature Furthermore, the interval determining the rate of change of log P need not be necessarily small. This is shown as follows: For the first substance

$$Q_1 = \frac{2.3\ RT^2\ \mathrm{d} \log P_1}{\mathrm{d}T}$$

and for the second substance

$$Q_2 = \frac{2.3\ RT^2\ \mathrm{d} \log P_2}{\mathrm{d}T}$$

Then at the same temperature the ratio of the heats of vaporization

$$\frac{Q_1}{Q_2} = \frac{2.3\ RT^2\ \mathrm{d}\log P_1}{2.3\ RT^2\ \mathrm{d}\log P_2} = \frac{\mathrm{d}\log P_1}{\mathrm{d}\log P_2} = \frac{\Delta\log P_1}{\Delta\log P_2}$$

By substituting the values for water for Q_2 and $\Delta \log P_2$ obtained from the International Critical Tables and our data for $\Delta \log P_1$ for intervals of 5°C. we calculated the heats of vaporization of water from the acid solutions. The values so obtained were next smoothed by plotting them as a function of the temperature. In drawing these curves it was borne in mind that the heat of vaporization for a solution must decrease at a rate not less than that for water. If this were not so the log P versus $1/T$ curve for a solution would intersect that for water at some temperature. Our smoothed heats were found to be represented by a linear equation whose constants are given in table 4. By means of this equation the heats of vaporization at a certain temperature may be calculated with an accuracy of approximately 1 per cent. Upon calculating the heats of vaporization from Greenewalt's table we concluded that his table was not sufficiently accurate to show the required decrease with temperature.

SUMMARY

A redetermination of the aqueous partial pressures over aqueous sulfuric acid solutions has been made for concentrations up to 70 per cent H_2SO_4 from 20°C. to 140°C. For this purpose an isoteniscope was devised which could measure vapor pressures of solutions with no accompanying change in the concentration of the solution. From the observed data a table of relative vapor pressures has been compiled, from which table it is possible to ascertain the aqueous partial pressure for aqueous solutions of sulfuric acid between 0 per cent and 70 per cent H_2SO_4 for any temperature from 20°C. to 140°C. inclusive. The heats of vaporization of water from solutions of the above range of concentration and temperature have been calculated and tabulated.

REFERENCES

(1) WILSON: Ind. Eng. Chem. **13**, 326 (1921).
(2) GREENEWALT: Ind. Eng. Chem. **17**, 502 (1925). And also International Critical Tables, Vol. III, p. 302. McGraw-Hill Book Co., New York (1928).
(3) HEPBURN: Proc. Phys. Soc. London **40**, 249 (1928).
(4) BURT: J. Chem. Soc. **85**, 1339 (1904).
(5) BRIGGS: J. Soc. Chem. Ind. **22**, 1275 (1903).
(6) SOREL: J. Soc. Chem. Ind. **9**, 175 (1890).
(7) REGNAULT: Ann. chim. phys. [3] **15**, 129 (1845).
(8) BRÖNSTED: Z. physik. Chem. **68**, 707 (1910).
(9) DIETERICI: Wied. Ann. **67**, 865 (1899).
(10) GROLLMAN AND FRAZER: J. Am. Chem. Soc. **47**, 715 (1925).
(11) HACKER: Ann. Physik [4] **39**, 1342 (1912).

(12) Smith and Menzies: J. Am. Chem. Soc. **32**, 1412 (1910).
(13) Thomas and Barker: J. Chem. Soc. **127**, 2820 (1925).
(14) Murray: Standards and Tests for Reagent Chemicals. D. Van Nostrand Co., New York (1920).
(15) Bur. Standards Bulletin No. 288.
(16) Burgess and Le Chatelier: Measurement of High Temperature, p. 121. John Wiley and Sons, New York (1912).

THE EFFECT OF DISSOLVED ELECTROLYTES ON THE BOUNDARY TENSION OF WATER

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It is often difficult to employ the capillary rise method for the determination of the interfacial tension of liquid–liquid interfaces. As a result of the work of Lohnstein (1) and of Harkins (2) on the modification of Tate's law, the drop volume method is probably the most precise and universally applicable substitute for use with this type of system.

When the drop volume method is used, the drops must form under as nearly equilibrium conditions as possible. This makes it necessary that the drops form entirely without outside assistance and that they form slowly, the maximum rate of drop formation depending on the time necessary for the attainment of interfacial equilibrium.

The purpose of the present study was to devise an apparatus for the convenient and accurate measurement of the interfacial tension of liquid–liquid systems, and to investigate the effect produced on the interfacial tension of such systems by various concentrations of the salts of the lower fatty acids. It was hoped that such measurements might throw some light on the boundary effects of strong electrolytes in solution.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus, a diagram of which is shown in figure 1, was constructed of Pyrex glass. It consists of a storage reservoir (R), from which either phase may be transferred either to the pipette (P) or to the flask into which the drops fall. The pipette is connected by a length of capillary tubing to the carefully ground glass dropping tip (T) by means of a ground glass joint. The tip was machined in a lathe and the dropping surface was made perfectly plane and perpendicular to the sides. The plane surface of the tip was roughened to insure complete wetting by the dropping liquid. The reservoir, pipette, and dropping flask were all connected so that a closed, isobaric system resulted. All connections were made by means of greaseless stopcocks and ground glass joints. By means of a threaded adjustment (A) attached to the top of the Pyrex needle valve (V), the speed of flow could be easily and reproducibly controlled.

The drops were caused to fall between two platinum electrodes (E) immersed in the oil phase. These electrodes were connected in series with a 1000-cycle tuning fork oscillator and the input of a vacuum tube amplifier using a UX280 rectifying tube and a UX210 amplifying tube. A diagram of the apparatus is shown in figure 2. The output leads from the amplifier were connected to the primary winding of a transformer, the ratio of which was 1600 to 1. The secondary winding of this transformer was connected in series with a specially constructed hot wire galvanometer (figure 3).

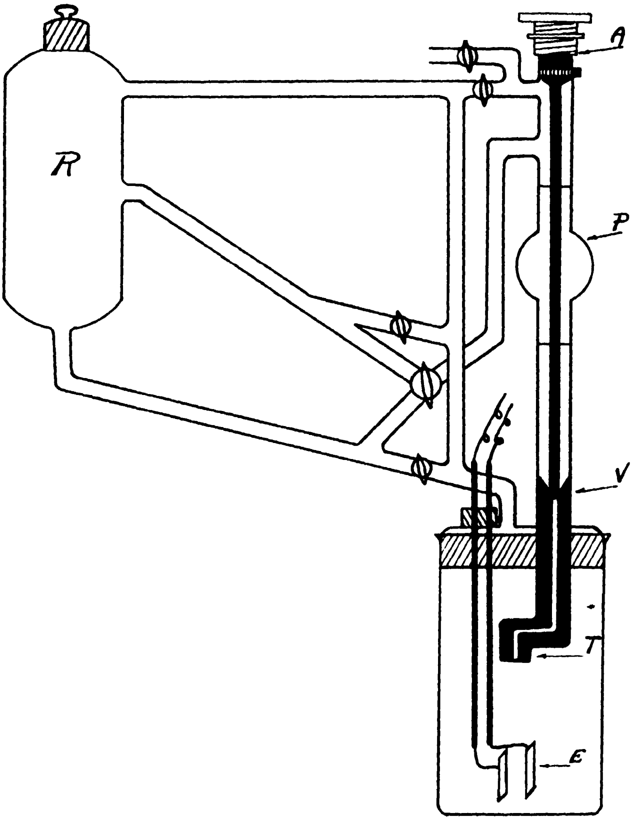

Fig. 1. Diagram of Interfacial Tension Apparatus

The galvanometer consisted of a length of No. 40 B & S gauge iron wire (W), one end of which was attached to a binding post and the other near the center of the balance wheel of an alarm clock. The clock framework was attached to the wooden support by means of flat steel springs (S). In order to relieve the small wire of the necessity of maintaining the tension between the clock framework and the support, and also in order to provide a compensator for variations in room temperature, a length of No. 20 gauge iron wire (C) was used. An aluminum wire (P) bearing a parchment paper pointer and a counterbalance (B) was attached to the balance wheel. The pointer serves as a marker on the slowly revolving smoked drum of a kymograph (K). The operation of the recording device depends on the heating effect of the amperage flux in the galvanometer circuit resulting from the passage of the drop of the aqueous solution between the electrodes.

The apparatus, with the exception of the recording device, was contained in a large, well-insulated air bath, the temperature of which was maintained at 40.00° ± 0.05°C. The air was stirred by means of an 8-inch fan which was suspended from springs supported from without the bath. Vibration was further reduced by placing the bath on a rubber foundation.

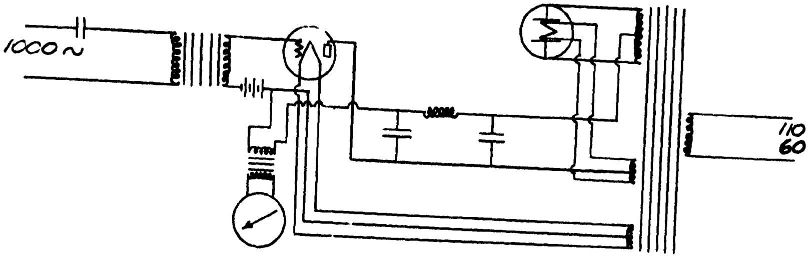

FIG. 2. WIRING DIAGRAM OF AMPLIFIER

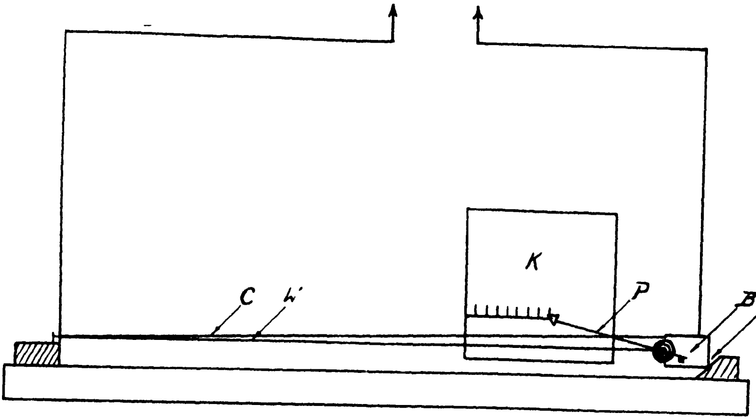

FIG. 3. DIAGRAM OF RECORDING DEVICE

The dropping pipette was carefully calibrated with both mercury and water at 40.00°C. The volume of the bulb between the calibration marks was found to be 21.1106 cc. The volume of the tube near the upper calibration mark was 0.3632 cc. per centimeter length, while the volume of the tube near the lower calibration mark was 0.3605 cc. per centimeter length. The height of the meniscus was read to 0.01 cm. by means of a cathetometer. The probable error in total volume is, therefore, of the order of

0.01 per cent. The diameter of the tip, measured by means of a precision micrometer, was 0.7042 cm.

When making a measurement of interfacial tension the two liquids were first thoroughly mixed at 40.00°C. and placed in the reservoir. From the reservoir the aqueous phase was transferred to the pipette and the oil phase to the dropping flask. The volume of liquid which flowed through the dropping tip was determined by reading the height of the meniscus immediately following the fall of the drop just preceding the first drop counted, and following the last drop counted. The needle valve was not adjusted after a run was once started.

The densities of the mutually saturated phases were determined at 40.00°C., using Ostwald type pyknometers with ground glass caps.

Mineral oil and toluene were used as the oil phases. The mineral oil was a good quality of medicinal oil. The toluene was washed with sulfuric acid and sodium hydroxide and was fractionally distilled. Only the middle fraction of the distillate, boiling between 109.8°C. and 109.9°C. at 748 mm., was used.

The salts were carefully purified by repeated recrystallization from conductivity water. Conductivity water was used in making up all aqueous phases.

RESULTS

The interfacial tensions were calculated by use of the Harkins modification of the equation of Tate,

$$\gamma = \frac{V(d_2 - d_1)\, g\, \Phi}{2\, \pi\, r}$$

in which V is the volume of the falling drop obtained by dividing the total volume of liquid by the number of drops, d_2 and d_1 are the densities of the aqueous and oil phases respectively, g is the gravitational constant, and r is the radius of the tip. Φ is the reciprocal of the Ψ function of Harkins which is the fraction of the pendant drop which falls from the tip. The values of Φ were read from a large graph of the data of Harkins (3) where Φ is plotted against $r/V^{1/3}$.

The data are tabulated in tables 1 to 4, and are shown graphically in figures 4 and 5.

The interfacial tension of mineral oil–sodium acetate systems decreases hyperbolically with increasing sodium acetate concentration from zero to 6 molal. Sodium formate, however, affects the interfacial tension quite differently in that there is a distinct minimum in the interfacial tension–concentration curve. At high concentrations of sodium formate the interfacial tension is greater than at zero concentration.

The interfacial tensions between sodium formate solutions and toluene

TABLE 1

The interfacial tensions of aqueous sodium acetate–mineral oil systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc*				*dynes per cm.*
0 00	0 50779	0 99222	0 83892	1.4928	51.52
0 05	0 48752	0 99454	0.83901	1.4972	50.34
0 10	0 45833	0 99607	0 83905	1 5060	48.05
2 04	0 28063	1 07150	0 83902	1 5600	45 14
6 12	0 18354	1 16845	0 83903	1.6090	43 13

TABLE 2

The interfacial tensions of aqueous sodium formate–mineral oil systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc*				*dynes per cm*
0 00	0 50779	0 99222	0 83892	1.4928	51 52
0 15	0 47054	0 99860	0 83904	1 5010	49 98
0 75	0 40181	1 02224	0 83902	1 5185	49.56
4 11	0 24295	1 12932	0 83902	1 5775	49 33
9 22	0 17435	1 24922	0 83906	1 6145	51 20

TABLE 3

The interfacial tensions of aqueous sodium acetate–toluene systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc*				*dynes per cm*
0 00	0 34863	0 99064	0.84027	1 5345	35 67*
0 10	0 30629	0 99866	0 84020	1 5515	33 39
1 02	0 27007	1 03382	0 84025	1 5645	36 27
2 04	0 22366	1 07325	0 84023	1 5871	36 68

* Value listed in International Critical Tables = 35.7.

TABLE 4

The interfacial tensions of aqueous sodium formate–toluene systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc*				*dynes per cm.*
0 00	0 34863	0 99064	0 84027	1 5345	35 67
0 75	0 27827	1 01315	0 84020	1 5605	33 31
3 00	0 19208	1 09135	0 84020	1.5800	33.80
9 22	0 11629	1 28660	0 84025	1 6483	37 94

when plotted against the concentration of the salt give a curve of the same type as that obtained when mineral oil was used as the oil phase. Against toluene the sodium acetate solutions also yielded an interfacial tension curve which passes through a very abrupt minimum.

The only value listed which may be strictly compared with accepted values is that of toluene against water. The International Critical Tables list the interfacial tension of this system at 40.00°C. as 35.7 dynes per centimeter, while three consecutive determinations with the apparatus described yielded values of 35.66, 35.67, and 35.67 dynes per centimeter.

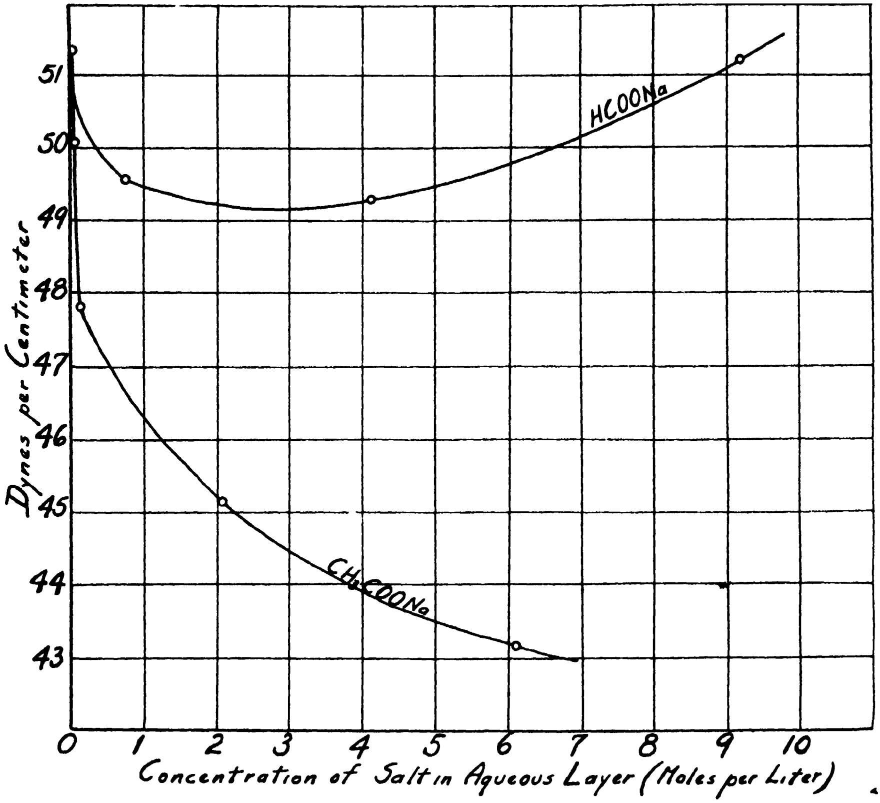

FIG 4. THE EFFECT OF SODIUM ACETATE AND SODIUM FORMATE ON THE INTERFACIAL TENSION OF WATER–MINERAL OIL SYSTEMS

DISCUSSION

The lowering of the interfacial tension of water–oil systems by low concentrations of salts of the lower fatty acids is to be expected, but the striking effect of high concentrations of these salts in raising the interfacial tension is a phenomenon which apparently has not been observed by previous workers. This type of behavior cannot be satisfactorily explained without some modification of the present theories of the surface effect of solutes. The results of Traxler and Pittman (3), which show exactly the same effect for sodium chloride on the interfacial tension of water–asphalt systems, suggest that the correct explanation will be based on the electrical forces acting between ions in the interface.

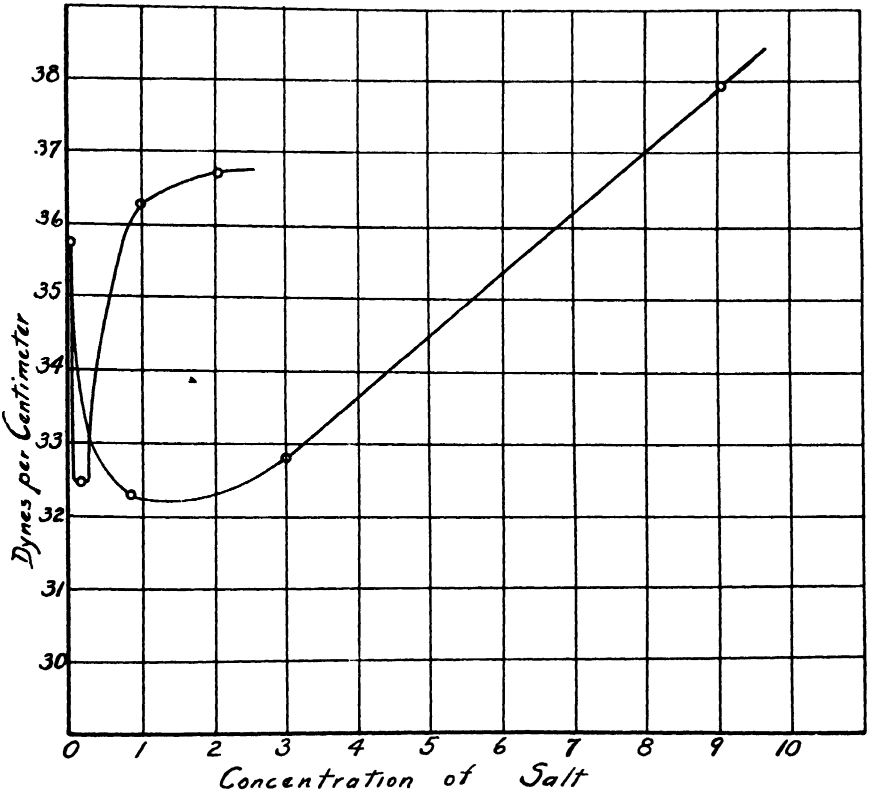

Fig. 5. The Effect of Sodium Acetate and Sodium Formate on the Interfacial Tension of Water–Toluene Systems

van der Waals in his accepted theory of surface tension at the liquid–vapor interface makes the assumption that the liquid and vapor phases are separated by a boundary layer of finite thickness in which the properties change gradually from those of the pure liquid on one side to those of the vapor on the other side. We may assume a similar boundary layer between two immiscible or partially miscible liquids. In this case, the two phases are the mutually saturated solutions, and the properties such as composition, density, and dielectric constant gradually change through an interfacial layer of finite thickness from those of one phase to those of the other.

According to the accepted theories of the surface effects of solutes, fatty acids or their ions orient themselves in the interfacial layer. Thus the acetate ions become concentrated in the interfacial layer, the hydrocarbon end tending to turn toward the oil and the carboxyl group toward the water. However, the exact location of the ions in the interfacial layer is determined as the resultant of three forces. The attraction of the oil phase for the hydrocarbon end of the ion tends to pull it up into the oil-like portion of the boundary layer. This force is opposed by the attraction of the water phase for the carboxyl end of the ion and by the electrostatic attraction of the sodium ion, which is hydrophilic and tends to remain in the water phase. Under a given set of conditions the acetate ions assume a certain equilibrium level in the interfacial layer, depending upon the equality of the opposing forces. Decreasing the concentration of the salt in the water phase increases the attraction of the water phase for the carboxyl group and shifts the equilibrium position toward the water-like side of the interfacial layer. On the other hand, increasing the concentration of salt decreases the attraction of the water phase for the carboxyl end of the ion, and the equilibrium position shifts toward the oil-like side of the interface.

The acetate ions and other fatty acid ions exert two opposing effects on the interfacial tension. By concentrating in the interface they decrease the attraction of the surface layer elements for each other and thus tend to decrease the interfacial tension as do the corresponding free fatty acids. On the other hand, oriented negative ions held at a certain equilibrium level in the boundary layer attract sodium or other positive ions into the boundary layer. The sodium ions occupy positions a little nearer the water side of the interface, each sodium ion occupying a mean position equidistant from two or more acetate ions. This effect gives rise to an increased attraction between the surface layer elements and, therefore, to an increased interfacial tension.

At low salt concentrations, the tension lowering effect predominates because, as pointed out above, the equilibrium position of the acetate ion is shifted toward the water side of the interface where the dielectric constant is high and the attraction between oppositely charged ions is correspondingly small. Furthermore, much of the effect at low salt concentrations may be due to free acid formed by hydrolysis. Undissociated free acid would have no tendency to raise the interfacial tension.

At high salt concentrations the acetate ions are shifted toward the oil-like side of the boundary layer. In this region, owing to the much lower dielectric constant, the attraction between the oppositely charged ions becomes much greater. For this reason, the tendency of fatty acid ions to increase the interfacial tension is greater at high concentration, and it may become even greater than the lowering effect, resulting in a system which has a higher interfacial tension than at zero salt concentration. Interfacial tension is defined as the work done in creating one square centimeter of fresh interface. It is evident that more work would be necessary if there were more closely attracted ions in the boundary layer.

On the basis of this hypothesis, the interfacial tension–concentration curves for sodium acetate and sodium formate would be expected to cross. At low concentrations the interfacial tension lowering should be greater for the acetate than for the formate, owing to the fact that the surface activity of the fatty acids increases with increasing molecular weight. At higher concentrations where the tendency of the ions to increase the interfacial tension becomes an important factor, the attraction of the oil phase for the hydrocarbon end of the ion would be greater for the acetate ion than for the formate ion. At equal surface concentrations, therefore, the equilibrium position of the acetate ion would be nearer the oil side of the boundary layer. This would lead to a greater increase in the interfacial tension of the acetate solution. Owing to the fact that the acetate ions are more highly adsorbed in the interface than the formate ions, the tendency of the sodium acetate to increase the boundary tension would be expected to appear at a lower total salt concentration.

The effect of most strong electrolytes in increasing the surface tension of water may be due to a similar type of effect. The less hydrophilic ion, or the ion which has the greater escaping tendency from the aqueous phase, would occupy a position in the boundary layer somewhat nearer the non-aqueous phase than would the more hydrophilic ion, the equilibrium position of both ions shifting toward the non-aqueous phase with increasing electrolyte concentration in the aqueous phase. Thus the same electrical forces which have been postulated in the case of the sodium acetate and sodium formate solutions would be set up in the boundary layer separating any aqueous solution of a strong electrolyte from a non-aqueous phase in which the electrolyte is practically insoluble. Under such conditions the tension raising effect of the electrolyte should increase with increasing concentration of electrolyte and with increasing difference between the hydrophilic properties of the two ions.

SUMMARY

By means of a specially designed apparatus the drop volume method of measuring interfacial tensions has been employed to yield very accurate results.

The effect of sodium acetate and of sodium formate on the interfacial tension of oil–water systems is very different from that of the free acids.

An attempt to explain the effect of these salts has been made on the basis of the Langmuir theory of molecular orientation and the increased inter-

ionic attraction in the interface due to the dielectric constant gradient in the interfacial layer.

The effect of strong electrolytes in general on boundary tension may be explained in a similar manner.

REFERENCES

(1) Lohnstein: Z. physik. Chem. **64,** 636 (1908).
(2) Harkins and Brown: J Am. Chem. Soc. **41,** 499 (1919).
(3) Traxler and Pittman: Ind. Eng Chem. **24,** 1003 (1932).

THE EFFECT OF SODIUM ACETATE ON THE INTERFACIAL TENSION OF THE BENZENE-WATER SYSTEM AT 40°C.

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A great deal of study has been made of organic liquid–aqueous solution interfaces by Reynolds (1), Harkins (2), Morgan (3), and others. In a recent publication by Eversole and Dedrick (4) it is shown that the sodium salts of formic and acetic acids affect the interfacial tension of water–oil systems in a rather unexpected way. It is shown that when the interfacial tension of the system is plotted against the concentration of the solute in the aqueous phase the curve obtained passes through a minimum and that at higher concentrations the interfacial tension is greater than at zero concentration.

The purpose of the present investigation was to extend the previous work (4) to other systems in an attempt to ascertain whether or not the effects noted in it are general.

APPARATUS AND MATERIALS

The apparatus is essentially that used in the work described above (4) except that it has been much simplified and that refinements have been made in the drop counting device. The diagram of the apparatus is shown in figure 1. It consists of a storage reservoir (R) from which the aqueous phase is transferred to the pipette (P) by suction. From the pipette, the solution passes through a needle valve (V) to the tip (T) from which it drops while at equilibrium with the oil phase contained in the dropping flask (F). The speed of flow was controlled by the screw adjustment (A) attached to the top of the needle valve. The dropping tip was ground perfectly flat and perpendicular to the bore of the tube, after which the surface was roughened slightly to insure complete wetting by the liquid phase dropping from it. The tip is removable and is connected to the pipette by a ground glass joint (S). Greaseless stopcocks and ground glass joints were used in all parts of the system.

The apparatus is mounted in a constant temperature air bath which was kept at 40.00° ± 0.05°C. All adjustments were made and the pipette refilled from outside the bath so that duplicate runs were made without the necessity of opening the thermostat.

The drop counting device is based on the same principle as that used in the previous work (4). An improved amplifier and a standard Fries weather recording device (figure 2) were used. With this apparatus a continuous twenty-four hour inked record could be made without attention from the operator. The current for operating the recording device is controlled by a sensitive relay which is connected in the plate circuit of the amplifying tubes.

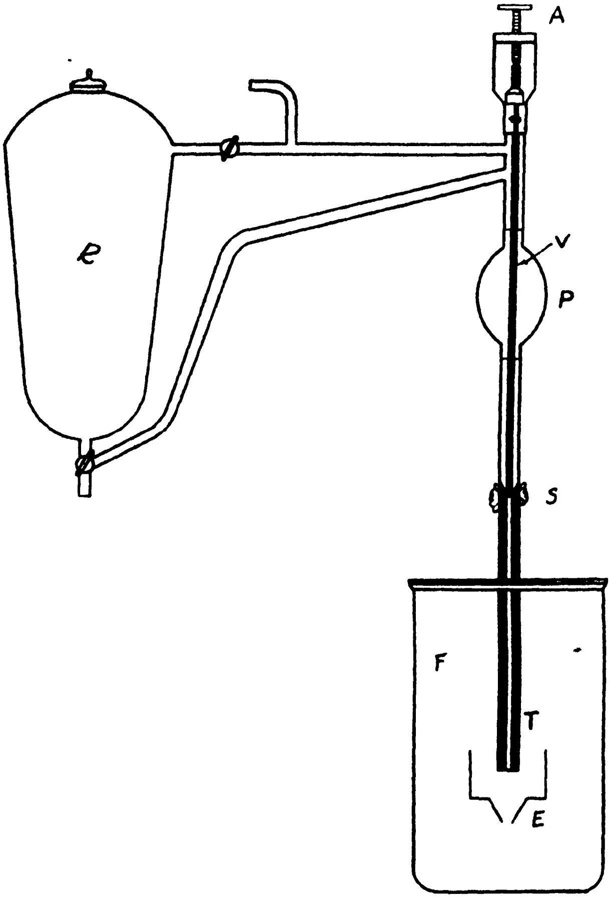


FIG. 1. DIAGRAM OF INTERFACIAL TENSION APPARATUS

The diameter of the dropping tip was carefully measured with a micrometer and found to be 0.9156 cm. The volumes of the pipette between the calibration marks and of unit length of the tubing above and below the calibration marks were determined at 40°C. with mercury and with water. The level of the meniscus was read to 0.01 cm. by means of a cathetometer which was placed outside the thermostat. Using the results of several measurements, all possible combinations of two simultaneous equations of the following form

$$l\frac{dV}{dl} + V_b = V_t$$

were solved for the values of V_b and dV/dl. In the above equation, l is the distance between the initial and final heights of the meniscus minus the distance between the calibration marks, dV/dl is the volume per unit length of tube near the calibration marks, V_b is the volume of the pipette between the calibration marks, and V_t is the total volume of liquid run out during the calibration. The total volume was determined from the weight and density of the liquid. The error in total volume is probably less than 0.01 per cent.

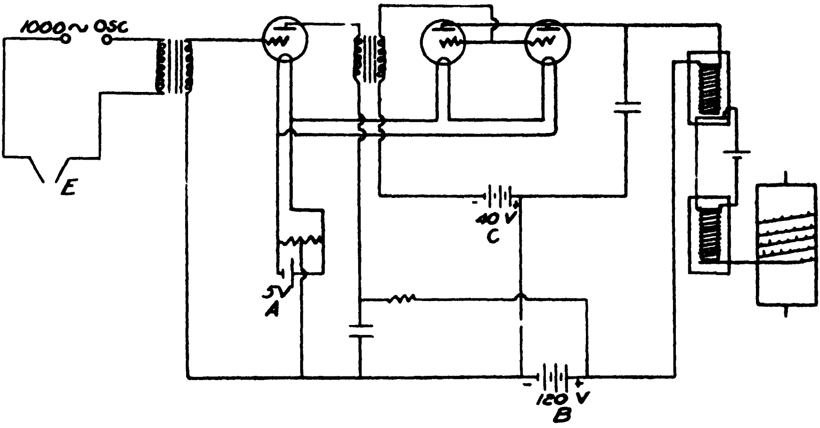


FIG. 2. DIAGRAM OF AMPLIFIER AND RECORDING DEVICE

The benzene was of standard quality and free from thiophene. Only the middle fraction boiling at 79.8°C. at a pressure of 741 mm. was used. The sodium acetate was Baker's analyzed product which had been twice recrystallized from conductivity water. All solutions were made using conductivity water as a solvent.

RESULTS

Experimental measurements and calculations were carried out in the manner described in the previous paper (4). Experimental results are given in table 1 and shown graphically in figure 3.

At very low concentrations the interfacial tension of benzene–sodium acetate systems decreases markedly with increasing concentration of the salt. After passing through a decided minimum at about 0 1 molal, the interfacial tension increases quite abruptly with a small increase in concentration. It then passes through a maximum, the value of which is greater than the initial tension between benzene and water. It then decreases hyperbolically as the solution becomes more nearly saturated.

TABLE 1

The effect of sodium acetate on the interfacial tension of the benzene–water system at 40°C

SALT CONCENTRATION	DROP VOLUME	$d_2 - d_1$	Φ	γ
molal	*cc*			*dynes per cm*
0 0000	0 46263	0 13342	1 5967	33 85
0 1458	0 42956	0 13968	1 6036	32 80
1 0555	0 38010	0 16419	1 6129	34 32
2 3505	0 31431	0 20415	1 6324	35 71
3 6572	0 25835	0 24465	1 6485	35 52
4 1074	0 24614	0 24540	1 6523	34 02
5 4112	0 21195	0 27915	1 6608	33 50
7 1167	0 17047	0 33667	1 6680	32 64

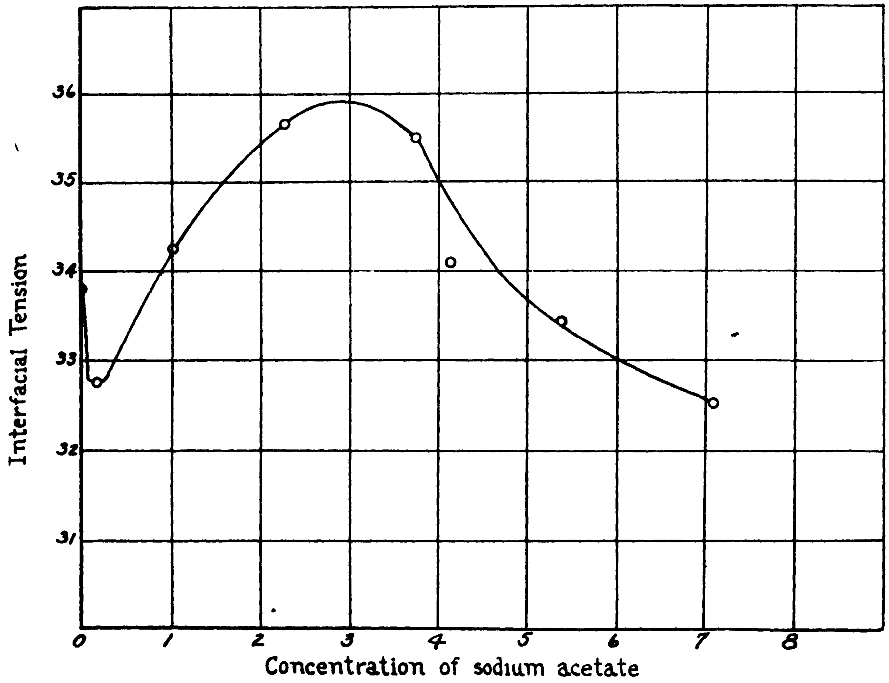


FIG 3. THE EFFECT OF SODIUM ACETATE ON THE INTERFACIAL TENSION OF WATER–BENZENE SYSTEMS

The only value obtained which may be strictly compared with accepted values is that of benzene against water. The value listed in the International Critical Tables for this system at 40°C. is 33.84 dynes per centimeter. The data presented herewith show the interfacial tension of this system to be 33.85 dynes per centimeter.

DISCUSSION

The effect of sodium acetate on the interfacial tension of the water–benzene system may be satisfactorily explained by the theory advanced in the previous paper (4) for sodium acetate concentrations less than approximately 2.5 molal. However, the secondary interfacial tension lowering at higher sodium acetate concentrations is a phenomenon which was not encountered in the previous work, probably because the measurements with sodium acetate in the water–toluene systems were not extended to sufficiently high concentrations.

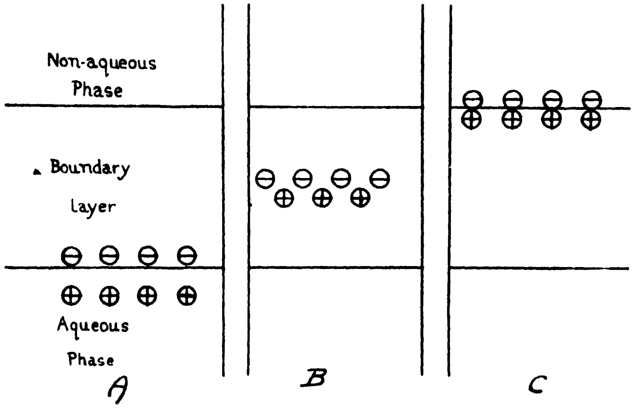


FIG. 4. DIAGRAM OF MEAN POSITIONS OF EFFECTIVE IONS IN BOUNDARY LAYER

This secondary lowering effect is probably due to the fact that the ions in the boundary layer approach or enter the oil phase as the concentration of salt in the aqueous phase is increased. In this region, the ions tend to form doublets, owing to their greater electrostatic attraction for each other in the medium of much lower dielectric constant. When the tendency to form doublets becomes sufficiently pronounced, the salt in the boundary layer behaves essentially as a surface active non-electrolyte, lowering the interfacial tension. While other ions are present in the water-like portion of the boundary layer, it is probable that their distribution is sufficiently random to prevent any considerable increase in boundary tension due to their presence.

The theory advanced in this and the previous paper (4) to explain the effect of strong electrolytes on the boundary tension of two phase systems is indicated in a purely diagrammatic way in figure 4. In this figure *A* indicates the postulated mean positions of the effective ions which result in the initial boundary tension lowering, *B* indicates their mean positions for elevation of the boundary tension, and *C* represents their mean positions when the secondary lowering is produced at high concentrations.

It is to be expected that the salt concentration at which the minimum and maximum in the interfacial tension-concentration curve occur, and, therefore, the concentration at which the secondary lowering begins, decreases as the tendency of the negative ion to pass into the non-aqueous phase increases. This statement is borne out by the results given in the previous paper (4) on the water-toluene system. Thus in dealing with the sodium salts of the fatty acids, the positions of the minimum and of the maximum points on the curves would shift to lower salt concentrations as the molecular weight of the fatty acid ion is increased. This is probably the reason that a similar type of effect has not been discovered for the soaps on the boundary tension of water-vapor and water-oil systems. The minima and maxima probably occur at such low concentrations that only the secondary lowering effect has been observed. The fact that the negative ions of the soap polymerize to form colloidal particles should not affect the mechanism of the boundary effect. The greater tendency of acetate ions to pass into mineral oil rather than into toluene or benzene may explain the failure to observe a minimum and a maximum in the sodium acetate curve for the water-mineral oil systems in the preceding work (4).

In general the concentration at which the minimum and maximum occur in any given system would be expected to increase with rising temperature, owing to the increased thermal agitation of the ions in the boundary layer.

It seems probable that this proposed mechanism will be sufficient to explain the effect of all strong electrolytes on the boundary tension of their aqueous solutions. Thus, any solute which is a strong electrolyte when dissolved in water will cause the initial lowering of interfacial tension and the subsequent increase at higher concentrations, provided one ion has a greater tendency than the other to leave the aqueous phase and go into the non-aqueous phase. This is strikingly illustrated by the results of measurements by Traxler and Pittman (5) of the effect of dissolved sodium chloride on the boundary tension of water-asphalt systems. Failure to observe this effect for many other electrolytes is probably due to the fact that careful measurements have not been extended to sufficiently low concentrations.

After the initial decrease and subsequent increase in boundary tension, the effect of strong electrolytes at still higher concentrations depends on an additional factor. This factor is the tendency of the electrolyte as a whole to pass through the boundary layer into the non-aqueous phase as doublets or undissociated molecules. If this tendency is appreciable, the secondary lowering effect will be obtained. Otherwise, the boundary tension will continue to rise with increasing electrolyte concentration in the aqueous phase. Thus, salts of most organic acids probably give the secondary lowering effect at the water organic liquid boundary on account of their tendency to pass into the organic liquid as undissociated molecules. Salts of organic acids which are very soluble in water probably do not give the secondary lowering effect at the water-vapor boundary. However the soaps do give this effect, owing to their tendency to form a third phase on the vapor side of the boundary layer.

Of the inorganic electrolytes, hydrogen chloride, hydrogen bromide, hydrogen nitrate, hydrogen sulfate, and other electrolytes which tend to pass into the vapor phase as undissociated molecules, exhibit the secondary tension lowering effect at the water-vapor boundary at high concentrations. Non-volatile electrolytes, including practically all salts, increase the surface tension of water at high concentrations. The increase, as has been mentioned previously, depends on the difference between the tendencies of the two ions to leave the aqueous phase as ions.

Other phases of the problem of boundary phenomena are being investigated as rapidly as is possible both in this laboratory and at the State University of Iowa.

SUMMARY

1. Accurate measurements have been made of the effect of dissolved sodium acetate on the interfacial tension of the water-benzene system.

2. The curve obtained by plotting the interfacial tension of this system against the concentration of sodium acetate shows, at high concentrations, a secondary tension lowering effect which has not been observed in previous work.

3. The theory of Eversole and Dedrick has been extended to include the boundary effects of strong electrolytes at higher concentrations.

4. The effects noted in this work appear quite analogous to those described by Taylor (6) in his theory of activated adsorption of gases by solids.

The authors wish to express their sincere appreciation for the very valuable suggestions and criticisms given by Dr. W. G. Eversole of the State University of Iowa.

REFERENCES

(1) Reynolds: J. Chem. Soc. **119**, 466 (1921).
(2) Harkins and Zollman: J. Am. Chem. Soc. **48**, 69 (1926).
(3) Morgan: J. Am. Chem. Soc. **33**, 349 (1911).
(4) Eversole and Dedrick: J. Phys. Chem. **37**, 1205 (1933).
(5) Traxler and Pittman: Ind. Eng. Chem. **24**, 1003 (1932).
(6) Taylor: J. Am. Chem. Soc. **53**, 578 (1931).
Taylor and Sickman: J. Am. Chem. Soc. **54**, 602 (1932).

NEW BOOKS

L'Architecture de l'Univers. By P. Couderc. Paris: Encyclopedie Gauthier Villars, 1930.

As the title indicates, the present volume, No. 6 in the series, attempts to describe the structure of the visible universe, but a glance at the table of contents indicates that the development of the universe also is included—in its widest cosmogonical aspects. It is not meant as a text book, and indeed it more resembles a collection of selected chapters, the first of which, without much preliminary, really disposes of the question of the structure of our Milky Way system.

A second chapter is devoted to a description of methods, terminology, and some related chemical and physical facts and laws. Chapter III treats of the spectral classification in detail and more specifically of the now defunct theory of stellar evolution, while chapter IV continues this with the Laplace-Jeans theory of the evolution of spiral nebulae, and Jeans's tidal theory for the origin of the planets. With a rather prolonged excursion into the geological evidence for the age of the earth, the probable ages of the stars and the time scale of the universe derived from double stars and clusters are discussed. This naturally leads to relativity, and its bearing upon astronomical space and cosmogony. The last two chapters deal with cosmic rays and the problem of life outside the earth.

The work is illustrated by eight excellent full-page photographs of star fields, clusters, and spiral nebulae. The principal criticism that might be advanced against it is that nearly all theories are presented as if they were final, without much comment or critical analysis. Thus, on p. 144 it is stated quite calmly that epidemics of "grippe" on the earth may well have a *cosmic* origin. An unfortunate slip on p. 103 states that the *inclination* of the earth's axis on the ecliptic varies in 26,000 years, and this may explain the periodic return of glacial epochs.

W. J. Luyten.

Annual International Tables of Constants and Numerical Data, Chemical, Physical, Biological, and Technological. Paris: Gauthier Villars et Cie. New York: McGraw-Hill Book Co., Inc.

Volume VIII, Literature of 1927–28 (published 1931–32) 4-to Part I. xl + 1101 pp. Part II. xxi + 1102–2706 pp. Cloth.

Volume IX, Literature of 1929 (published 1931) 4-to i + 1607 pp. Cloth.

Numerical Data of Spectroscopic Literature of 1925–26. (Extract from Vol. VII of Annual International Tables) (published 1930). 4-to xix, 414–927 pp. Boards.

Index to volumes of the 1st series (I to V, 1910–1922) (published 1930). Compiled by G. Kravtzoff. 4-to lxii + 382 pp. Cloth.

Index to Volume IX. Literature of 1929 (published 1932). Compiled by G. Kravtzoff. 4-to xxiv + 124 pp. Boards.

These volumes represent a continuation of the activities of an International Committee appointed by the 7th Congress of Applied Chemistry (London, 1909) and continued under the auspices of the International Research Council and the International Union of Chemistry. Dr. Ch. Marie, Secretary General of the International Committee, has unstintingly devoted his energies to the task of making this project a success, and he merits the sincere thanks of all workers in the field of the chemical and physical sciences.

The scope of the work as represented in the earlier publications is so well known to scientists that an extended review of the present volumes is unnecessary. In these days when scientific data are scattered through a thousand "journals" it becomes imperative that someone undertake the task of collecting those data which appear to possess more or less permanent value and making them available to the researcher in some such form as those publications represent.

It is a necessary consequence of this type of publication that volumes such as these should be rather expensive. However, their cost would represent an insignificant fraction of the cost of the time which the industrial or research worker without them would spend in searching the literature, so that the initial cost for their purchase will eventually be returned manyfold. It is an interesting commentary on human nature that the governing body of an organization will often quibble over a very moderate expenditure for books and at the same time spend without a question thousands of dollars for machinery, equipment, or new personnel. The library is the heart of a university or of a research laboratory, and volumes such as these are an invaluable adjunct to abstract journals.

Special attention should be called to the index volumes, the first being a collective index for Vols. I to V. More than twenty thousand substances are classified here. It contains (1) an analytical index alphabetically arranged in four languages (in parallel columns), (2) an alphabetical index of all substances (animal, plant, mineral, technologic products, etc.) including many chemical "trade names" which the chemist does not always associate with the chemical formula, and (3) a formula index, (arranged according to empirical formulas) of all definite chemical compounds.

These volumes, and those which preceded and those which will follow, should be on the shelves of every reference library and of the library of every research institution. Special prices may be secured by taking advantage of the subscription rates. Incidentally, it may be noted that certain sections (note, *e.g.*, section on spectroscopic data noted above) may be purchased separately if purchase of the entire volume is not desired.

Ross Aiken Gortner.

Einfuhrung in die Elektronik. By O. Klemperer. 25.5 × 17 cm.; xii + 304 pp. Berlin: Springer, 1933. Price: unbound, 18.60 marks; bound, 19.80 marks.

The sub-title is "The experimental physics of the free electron in the light of classical theory and of wave mechanics." The experimental side of the subject is stressed throughout, the mathematical and theoretical sides being merely quoted in sufficient detail to give point to the story. Problems involving relatively abstruse sections of electron-gas kinetic theory are handled either very briefly, or not at all; there is, for example, no mention of thermoelectricity.

So far as concerns the mere experimental side of our acquaintance with the properties of the negative electron, the book may not inaptly be described as a small "Encyclopaedia Electronica." It deals with a wide range of very diverse phenomena, here grouped for convenience—and of necessity somewhat arbitrarily—under three main headings: (1) the free electron; (2) electron emission; and (3) interaction between free electrons and atoms. The treatment, in a single volume of this size, is naturally not exhaustive (in the account of Millikan's oil-drop experiments, for instance, the question of the validity of Stokes' law is dismissed in a brief footnote), but the text is supplemented by well-chosen references to original papers.

The value of the work is enhanced, for many classes of readers, by the inclusion of a good selection of numerical tables, ranging from atomic structure factors to data on sensitivities of photographic emulsions to electrons of different speeds. The numerical data quoted are generally based on the most recent determinations of the relevant fundamental constants—though, as a minor criticism, it appears somewhat inconsistent to quote the round figure of 300 volts as the equivalent of 1 E.S.U. of potential difference, while stressing the distinction between absolute and international electrical units.

Taken as a whole, the book may be recommended as an excellent introduction to —and, for non-specialists, an adequate summary of—the greater part of experimental electronics. There was a real need for a compilation of this character, and Dr. Klemperer's book fills a very definite gap in the literature of his subject.

H. R. ROBINSON.

Actualités Scientifiques et Industrielles, 51 et 52. By M. G. URBAIN. Théories chimiques, publiées sous la direction de M. G. Urbain. I et II. La coördination des atomes dans la molecule; la symbolique chimique. 51 and 52 pp. Paris: Hermann et Cie, 1933. Price: 12 francs each.

In this beautifully and clearly written monograph, Professor Urbain, using a historical background, attempts to bring the theories of inorganic and organic chemists about the structure of chemical compounds to a common basis. In general, he thinks that the theories of structure in inorganic chemistry have rested on a molecular *pluraliste* basis, beginning with the electrochemical theory of Berzelius, and, after that was abandoned following the discovery of substitution by Dumas, revived in a modified form many years later in the coordination theory of Werner.

He thinks of the structures of organic chemists as referring everything to attractions between atoms without any thought of electrical forces, beginning with the substitutions of Dumas, through the types of Gerhardt—Laurent is not mentioned—and the atomic linkings of Kekulé. Frankland and Couper are omitted but a complete picture is not to be expected in so brief a monograph.

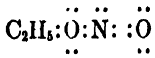
Professor Urbain sums up his conclusions in three sentences, (p. 40, Part II): (1) Neutral molecules may be formed with electrovalent unions. (2) Neutral molecules may be formed with non-electrovalent unions. (3) When a molecule contains both electrovalent and non-electrovalent unions, such a molecule should be considered as a complex molecule in which the constituent parts belong to the first two classes.

Among the "electrovalent" unions Professor Urbain includes the union between hydrogen and carbon in methane and many other unions which American and English chemists consider as covalent. He thinks of the electron as transferred from the hydrogen to the carbon and that there is hidden *dissimule* ionization in such cases (Part I, p. 26; Part II, pp. 19 and 21). In this he follows, without knowing it, the interpretation of Kossel's electronic theory, which has been made the basis of articles in the Chemisch Weekblad by van Arkel and de Boer, published in a German translation. Such a point of view confuses covalences with genuine ionic valences, though the latter may be found in compounds in "semi-ionic" unions and in complex molecules.

Closely connected with this confusion is his failure to see (Part I, p. 32 and elsewhere), that Meisenheimer has demonstrated that the fourth and fifth valences of quinquevalent nitrogen are different. The fourth is a covalence similar to the three covalences of ammonia, while the fifth is a positive ionic valence.

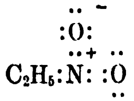
In a similar manner (Part I, p. 49), while he sees clearly that if the chlorine of triethylsulfonium chloride is united by a covalence to the sulfur atom that atom would have ten instead of eight electrons in its outer shell, he has not understood that when a sulfur atom takes on a third covalence it becomes a positive ion, just as the nitrogen of ammonia becomes a positive ion when it takes on a fourth covalence.

It was hardly to be expected that Professor Urbain should know that alkyl nitrites and the isomeric nitro compounds have quite different electronic structures. Ethyl nitrite is



$$C_2H_5:\overset{..}{\underset{..}{O}}:\overset{..}{N}:\,:\overset{..}{\underset{..}{O}}$$

and boils at 17°C. Nitroethane is



$$\begin{array}{c} \overset{..\ -}{:O:} \\ C_2H_5:\overset{..+}{N}:\,:\overset{..}{\underset{..}{O}} \end{array}$$

and boils at 114°C. This makes his reasoning about the structure of these compounds fallacious (Part II, p. 26). Silver nitrite gives, with alkyl halides, alkyl nitro compounds by an electronic and molecular rearrangement.

The author of the monograph seems (Part II, pp. 36–39) to confine the term "non-electrovalent" to bonds between atoms of the same kind. He is unable to furnish any definite electrical or electronic interpretation of such bonds. van Arkel and de Boer, in the book referred to, acknowledge the same difficulty. The theory of shared electrons proposed by G N. Lewis in 1916 gives a very satisfactory explanation for this difficulty, and that theory has been given a kinetic interpretation by Noyes, Campbell, Sidgwick, C. A. Knorr, and others, and a quantum mechanics interpretation by Slater, Linus Pauling, and others. That theory enables us to foresee, instead of a single neutral methyl discussed by Urbain, three kinds of methyl for which there is good experimental evidence: positive methyl formed by the ionization of methyl iodide when the methyl adds to the sulfur atom in the formation of trimethylsulfonium iodide; neutral methyl with an odd electron formed by the electrolysis of sodium acetate and by dissociations; and negative methyl, formed by the ionization of one of the bonds of ethylene to permit the positive chlorine of hypochlorous acid to unite with it while the negative hydroxyl unites with the positive methyl.

The most serious criticism of the book is the failure to make any reference to the theory of coördination proposed by Sidgwick, who ascribes it to covalences in his book on "The Electronic Theory of Valency." Professor Urbain comes surprisingly close to this when he compares the stereochemistry of the optically active compounds of carbon with that of the optically active complexes. His ideas of non-electrovalent structures prevent him from reaching a satisfactory conclusion. Sidgwick has presented an electronic theory based on that of Lewis and Langmuir which makes it applicable to all the chemical elements and all compounds. A somewhat modified exposition of that theory of inorganic complexes will be presented soon in The Journal of the American Chemical Society by the author of this review.

W. A. Noyes.

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